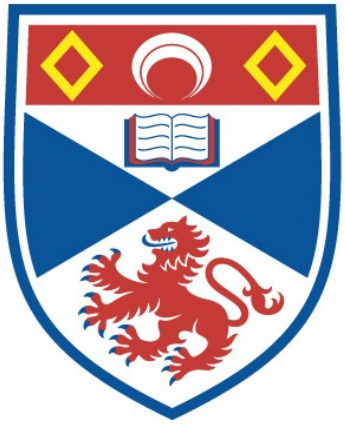
THE REACTION BETWEEN TOLUENE AND DEUTERIUM CATALYSED BY SOME METALS OF GROUP VIII

Richard Bell Moyes

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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THE REACTION BETWEEN TOLUENE AND DEUTERIUM CATALYSED BY SOME METALS OF GROUP VIII

being a thesis presented by

RICHARD BELL MOMES B.Sc.

to the

UNIVERSITY OF ST. ANDREWS

in application for the

DEGREE OF DOCTOR OF PHILOSOPHY

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DECLARATION

I hereby declare that the following thesis is a record of results of experiments carried out by me; that it is my own composition; and that it has not been previously presented in application for a Higher Degree.

The experiments were carried out in the Chemical Research Laboratories of St. Salvator's College under the direction of Dr. Charles Horrex.

CERTIFICATE

I hereby certify that Richard Bell Hayes B.Sc. has spent ten terms at Research Work under my direction, that he has fulfilled the conditions of Ordinance No. 16 (St. Andrews), and that he is qualified to submit the accompanying thesis in application for the Degree of Doctor of Philosophy.

Director of Research

UNIVERSITY CAREER

I entered St. Salvator's College of the University of St. Andrews in October 1955, and graduated B.Sc. with First Class Honours in Chemistry in June 1959.

The researches described in this thesis were begun in June 1959, and continued during my appointment as Assistant in Chemistry from October 1960 until September 1964.

ACKNOWLEDGEMENTS

I would like to acknowledge my indebtedness to Dr. Charles Norrex for his guidance and assistance in all aspects of this work; and to thank Professor J.I.G. Cadogan for the provision of research facilities, and the Department of Scientific and Industrial Research for a Research Scholarship.

I should also like to thank Mr. T. Norris for constructional work and Mr. R. Norris for the photographs.

Section 1.1

Introduction

Catalytic action is usually held to be preceded by some form of chemical interaction of one reactant, or of both, with the catalyst. Toluene has certain distinctive features from this point of view. The carbon-hydrogen bond dissociation energy for the side chain bonds is about 84 kcal. mol^{-1} while the ring carbon-hydrogen bond energy is probably greater than 105 kcal. $mole^{-1}$.[1] The side chain gives aliphatic characteristics while the aromatic ring of toluene adds the further possibility of interaction with the catalyst through its unsaturated properties and, as a special aromatic feature, through the π-ring system. It was the possible interplay of these features which suggested this research.

The brief literature survey deals with general features of the exchange reactions of saturated hydrocarbons, unsaturated and aromatic compounds only in so far as the main features are judged to have a bearing on the toluene problem and to show the development of features common to most exchange reactions.

The catalyst metal was varied in the experimental part of this work and since this can be viewed as altering the nature of toluene's reaction partner some relevant similar work in the literature is summarised. Evaporated films of metal were chosen as catalytic agents in order to avoid possible complications arising from supporting materials and differing preparatory methods from metal to metal. Wherever possible work on metal film catalysts will therefore be used to provide the examples in the following literature survey.

Section 1.2

Exchange of deuterium with hydrocarbons

(a) Nomenclature

The question of nomenclature arises here. In the following pages

the term hydrogenation or deuteration will be used to describe the addition of hydrogen of the appropriate isotopic type to unsaturated systems. The term "exchange" will be used to describe replacement of one isotopic species of hydrogen by the other without otherwise altering the molecule. The term "hydrogens" may be used generally to describe mixtures of the two isotopes. Where toluene molecules contain deuterium of known amount but unknown position they will be referred to e.g. as toluene - d_6 inferring six hydrogen atoms have been replaced by deuterium atoms. Side chain deuterium may be referred to e.g. as toluene - α - d_3 where specific reference is required.

(b) Mechanism

The earliest investigations lead to the postulation of two mechanisms of exchange.

(1) The dissociative mechanism [2,3] in which the saturated molecule is dissociated into an adsorbed radical and a hydrogen atom at the catalyst surface. This inferred a stepwise exchange process, the desorbing radical taking with it a deuterium atom.

(2) The associative mechanism [4] in which an unsaturated molecule is held to the catalyst surface by "the opening of the double bond" in the form of an adsorbed diradical.

The intermediates formed in the above reactions may then desorb with a chemisorbed deuterium atom which is often termed the Langmuir [5] - Hinshelwood mechanism because of their development of ideas concerning dissociation of reactants on catalysts or, alternatively, the intermediates may then react with a gas phase or Van der Waals adsorbed deuterium molecule (Eley-Rideal mechanism [6]).

These early studies established that the exchange occurred much more readily than cracking of hydrocarbons despite the fact that carbon hydrogen bonds are substantially stronger than carbon-carbon bonds. With the techniques available at the time it was not possible to discover whether a

single hydrogen atom is replaced or whether more extensive exchange occurs during the lifetime of the hydrocarbon molecule on the surface of the catalyst. This type of information became available only after the mass-spectrometric technique of following exchange reactions was introduced.[7]

Section 1.2 c

Exchange of deuterium with simple saturated hydrocarbons

Using the mass-spectrometric technique Kemball and his co-workers set out to examine the reaction of hydrocarbons with deuterium. They have published[9] an extensive study of the exchange of methane on evaporated metal films.

The reaction on nickel films gave rise to all four deuterium-containing methanes in the initial products, CD_4 being the most abundant product at first.

The results obtained are explained by two mechanisms of exchange, one through a stepwise exchange in which one atom is exchanged for each adsorption on the surface:

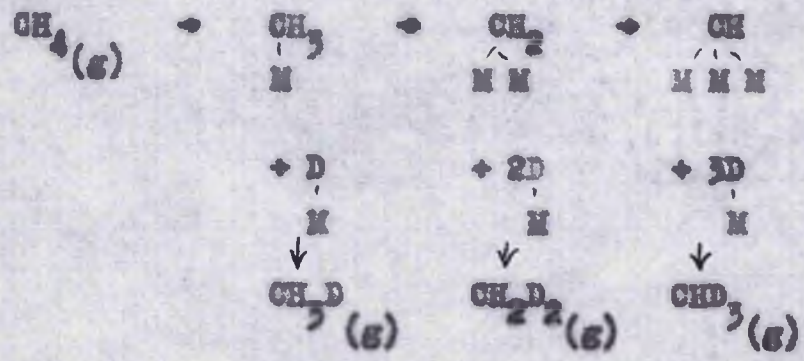
$$CH_4(g) \rightarrow \begin{matrix} CH_3 \\ | \\ M \end{matrix} + \begin{matrix} H \\ | \\ M \end{matrix}$$

$$\begin{matrix} CH_3 \\ | \\ M \end{matrix} + \begin{matrix} D \\ | \\ M \end{matrix} \rightarrow CH_3D(g)$$

$$CH_3D(g) \rightarrow \begin{matrix} CH_2D \\ | \\ M \end{matrix} + \begin{matrix} H \\ | \\ M \end{matrix}$$

$$\begin{matrix} CH_2D \\ | \\ M \end{matrix} + \begin{matrix} D \\ | \\ M \end{matrix} \rightarrow CH_2D_2(g) \quad \text{etc.}$$

The second is through a multiple exchange during one sojourn on the surface:



For this multiple exchange di- and tri- adsorbed species were postulated so that two or three deuterium atoms could be added for each sojourn on the catalyst. These species have been confirmed to some extent by Ashmore, Wright and Kemball [10], who determining the amount of hydrogen evolved when methane and ethane were chemisorbed on metal films. The rates of methane-deuterium exchange found by Kemball [9] up to 200°C increase roughly in proportion to the percentage "d" character of the metal although tungsten is more active and palladium much less active in multiple exchange than expected.[11]

Anderson and Kemball [12] examined the exchange of ethane on evaporated metal films. Consideration of the distribution of deuterium in the initial products again indicated multiple as well as stepwise exchange. The effect of changing the metal on the amount of multiple exchange is shown by the value of M, which may be obtained from the ratio of the rate of exchange to the rate of disappearance of initial hydrocarbon. A full definition of M is given in Section 3.2. M is the number of hydrogen atoms exchanged during one sojourn on the surface at the beginning of the reaction.

Metal	W	Mo	Ta	Pd	Rh	Zr	Cr	V	Pt
M	1.3	1.16	1.15	4.8	5.0	2.3	2.5	2.6	3.5

Ethane was thought to adsorb singly as an adsorbed ethyl radical, with loss of one hydrogen atom, or as a di-adsorbed "ethylene" molecule:

$$C_2H_{6(g)} \rightleftharpoons \underset{M}{C_2H_5} \rightleftharpoons \underset{M\quad M}{CH_2 - CH_2}$$

on desorption it could therefore take up one or two deuterium atoms, depending on the form from which it was desorbed.

An elegant interpretation of these complicated results involving the calculation of the likelihood of the molecule desorbing as ethane or re-adsorbing as di-adsorbed ethylene has been put forward. The percentage d character and crystal geometry have been used to explain differences in metal reactivities.

Propane is of interest as the molecule contains primary and secondary hydrogen atoms. The reaction has been studied by Kemball and his co-workers[13,14] on metal films of tungsten, rhodium, palladium and nickel. Multiple and stepwise exchange occurred. Rhodium and palladium films showed extensive multiple exchange which obscured the relative primary and secondary hydrogen reactivities. While the rates for primary and secondary hydrogen exchange were the same on tungsten, on nickel secondary hydrogen atoms exchanged ten times faster. As with ethane, the possibility of the adsorbed propyl radical becoming di-adsorbed arises and the following sequence has been suggested[15]:

$$CH_3 - \underset{M}{CH} - CH_3 \rightleftharpoons \underset{M}{CH_2} - \underset{M}{CH} - CH_3 \rightleftharpoons \underset{M}{CH_2} - CH_2 - CH_3$$

Experimental evidence suggests the isopropyl radical is the most easily

formed and this can undergo conversion through a di-adsorbed species to n-propyl radicals.

From the propane and ethane examples a general pattern of behaviour can be observed.[16] The inter-conversion between adsorbed alkyl radicals and di-adsorbed alkane molecules appears to be a general feature of exchange reactions of saturated hydrocarbons on metals. Rowlinson, Burwell and Tamaru[17] have termed this an α-β process because it involves adjacent carbon atoms. The work of Burwell and Briggs[18] on 3,3, dimethyl hexane and 2,2,3, trimethyl butane over nickel-kieselguhr catalysts established that exchange must occur by an α-β process as it is stopped by a quaternary carbon atom. This would be expected if the α-γ process is unlikely. Kemball[19] obtained results for neo-pentane on metal films, (the smallest molecule containing a quaternary carbon atom), and found that, as with methane, the exchange required a higher temperature than was required for the exchange of ethane. On palladium catalysts stepwise exchange occurred which compared well with the methane-deuterium reaction on these metals, while on nickel two or three hydrogens were replaced at one sojourn on the catalyst probably by an α-α process similar to that reported for methane.

Section 1.2.4

Exchange of deuterium with saturated cyclic hydrocarbons

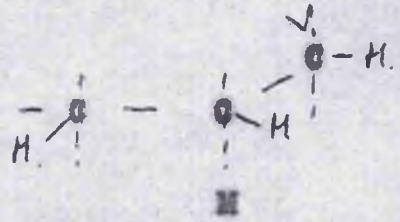
After these brief comments on the general pattern of exchange it is reasonable to jump to consideration of the reaction of deuterium with cyclic hydrocarbons partly because they are relevant to problems we meet in our experimental work because of the hydrogenation of toluene, and partly because they illustrate the development of a new theory concerning the type of bonding of the adsorbed intermediates to the catalyst surface.

Results obtained for cyclic hydrocarbons on metal films[21] and on supported metals[18] particularly for cyclohexane and cyclopentane show, from the initial distribution of deuterium in the products, that extensive multiple exchange has occurred and that half the hydrogen atoms are more

readily exchanged than the remaining hydrogen atoms. Anderson and Kemball [20] suggested that multiple exchange by an α-β process involving interconversion of adsorbed cyclealkane radicals and di-adsorbed cyclealkenes occurs. This α-β process can propagate around the ring on one side only and the ring then has to "turn over" before it can repeat the process on the other side. This mechanism occurs at lower temperatures and as the reaction temperature is raised the clear division in the distribution of products is removed. The "turnover" process was believed to occur through a di-adsorbed α-α radical although Burwell suggested an alternative.[21]

Multi point adsorption is a concept which produces considerable stereo chemical difficulties when attempting to reconcile the usual carbon-carbon distances with inter atomic spacings in catalysts. Kemball, Gault and Rooney [22,23] have suggested that hydrocarbons can be bonded to catalysts by interaction of the π electron system of a suitably unsaturated compound or molecular fragment with vacant d orbitals of the metal. Such a type of bonding is known to occur in ethylene platinous chloride, in π -allyl complexes,[24] or in ferrocene and bis-benzene chromium.

Their idea to explain the results with cyclohexane can be represented in the following way. Three carbon atoms of a chain or ring form an attached intermediate formulated as:-



Each carbon atom is Sp^2 hybridised, the dotted bonds represent the p electron distributions which can interact with the metal by entering into combination with surface orbitals. A relic of the formal bond approach used for ethylene is retained by suggesting that only one metal atom is

involved in the bonding, and this conveniently removes difficulties arising from interatomic distance disparities between adsorbent and adsorbate. It is clear that the above intermediate can be produced from a saturated compound by dissociation of hydrogen atoms from positions 1,2 and 3 or from an unsaturated compound by "opening of a double bond" plus the loss of a hydrogen atom. Kemball et al have emphasised that the attached intermediate is essentially planar and that addition of deuterium might occur from above or from below during the catalysed exchange. This affords one method of explaining stereochemical inversions of configuration which accompany exchange in some instances.

Rooney[24] has exchanged 1,1,3,3 tetramethyl cyclohexane in which the carbon atoms in positions 4,5 and 6 on the ring could form an allyl intermediate when three hydrogen atoms are lost. The resulting species is bound to the catalyst through the delocalised p orbitals. Exchange can occur at positions 4 and 6 involving inversion but not at position 5, except on desorption. Thus both atoms on 4 and 6 positions can be exchanged, but only one at position 5. For stereochemical reasons these three atoms will be the first to undergo exchange so we would expect a maximum in the initial distribution of deuterium at the d_5 compound. This is found at temperatures low enough to ensure that no exchange has occurred at the alternative positions.

These π -bonded intermediates are a useful species for explaining some of the features of exchange not otherwise explicable by the behaviour of the earlier α-β di adsorbed intermediate. (inversion, cis-trans isomerisation etc.) The full ramifications of such ideas have still to be explored and these early papers contain some inconsistencies. The importance of such intermediates in considering the toluene-deuterium exchange system is clear; many workers have readily accepted this type of bond in the explanation of exchange with aromatic compounds which will be discussed below.

Section 1.2 e

Summary

The results can be summarised for all saturated hydrocarbons as [16]

1. Hydrocarbons are apparently adsorbed as alkyl radicals or α-β di-adsorbed alkene radicals or π bound complexes. This gives rise to stepwise and multiple exchange, their relative ratio depending on the metal catalyst used. The distribution of deuterium in the initial products [15] the method of determining the extent of multiple exchange, along with M, the ratio of rate constants.

2. Adsorbed alkyl radicals are less easily formed from methane or methyl groups attached to a quaternary carbon atom in larger molecules. More highly dissociated species can be formed from these molecules but this usually requires additional activation energy.

3. α-γ di-adsorbed radicals are rarely formed and only at relatively high temperatures and consequently an exchange process cannot propagate past a quaternary carbon atom.

4. Hydrocarbons can be grouped [7] in descending order of reactivity in terms of the relative ease of exchange of different hydrocarbons on the same metal.

(a) Cyclic hydrocarbons, cyclopentane greater than cyclohexane
(b) ethane less than propane and iso butane
(c) neo-pentane
(d) methane

Section 1.2 f

Exchange of deuterium with unsaturated hydrocarbons

The attention of investigators has been directed to some of the same points as for saturated hydrocarbons - the kinetic analysis of the reaction and the type of deutero-compounds produced as the reaction proceeds,- but with unsaturated hydrocarbons there exists the further

interest of a comparison of the processes of exchange and hydrogenation. It was recognised by the early workers on exchange processes that unsaturated hydrocarbons might become attached to the catalyst by dissociation of C-H bonds and adsorption as radicals and hydrogen atoms, or use could be made of the reactivity of double bonds to give di adsorbed radicals. Clearly a configuration $\overset{M}{CH_2}\text{-}\overset{M}{CH_2}$ would be the same whether produced by dissociation of two C-H bonds in ethane or by adsorption of ethylene, and the conceptual inter-relationship of the reactions $D_2 + C_2H_4$ and $D_2 + C_2H_6$ is clear. Horiuti and Polanyi [4] envisaged the above configuration as being transferred to a "half hydrogenated state" $\overset{M}{CH_2}\text{-}CH_2D$, which is effectively an adsorbed ethyl radical, and that this state could either revert to $\overset{M}{CH_2}\text{-}\overset{M}{CHD}$, or desorb as C_2H_5D or $C_2H_4D_2$ by acquisition of a further H or D atom. More than a quarter of a century later Kemball [16] still uses a formulation:-

Gaseous ethylene $\overset{a}{\underset{b}{\rightleftharpoons}}$ adsorbed ethylene $\overset{c}{\underset{d}{\rightleftharpoons}}$ adsorbed ethyl radical $\overset{}{\rightarrow}$ gaseous ethane

Kemball, however brought to bear on the problem analytical data provided by mass spectrometry to assess the relative proportions of reactions c and d which occur on different surfaces and, as with saturated hydrocarbons, has emphasised the value of studies to initial rates of formation of the various deuterium-containing species. In dealing with his reaction scheme he attempted to assess the relative probabilities of his processes a to d from the analytical data. Differences between the behaviour on various metals were ascribed to changes in these relative probabilities. For example on tungsten a low chance of an ethyl radical reverting to an ethylene molecule (process c) increases the relative yield of ethane. Information of the exchange reaction of higher olefins is very sparse [15] compared with that available for ethylene and this field is at the moment undergoing a reappraisal in terms of the mechanism involving π bonded intermediates. [22,23] In Kemball's view the necessary conditions for formation of this kind of intermediate are that there should be not less than three adjacent non quaternary carbon atoms. Rooney considers

π bonding possible with one double bond. The exchange reaction of olefins is so different from that of aromatic hydrocarbons that only a small amount of space will be devoted to it here.

Section 1.2 g

The exchange reaction between deuterium and aromatic hydrocarbons

The exchange reaction between benzene and deuterium has been studied on metal films by Anderson and Kemball [26] and as this presents a near parallel to the present work it will be examined in detail. The exchange reaction was too fast to be measured over nickel films at -45°C and over iron films at 0°C although deuteration rates were slow and measurable. Silver films catalyse exchange at 295 to 375° without causing deuteration. Palladium and platinum gave rise to exchange and deuteration reactions in the temperature range 18 to 80°C and -44 to 0°C respectively and there was evidence that the two reactions were completely independent. The distribution of cyclohexanes formed at any stage in the course of the reaction indicated that deuteration involved pure addition without exchange. The evidence that deuteration and exchange are independent processes comes from a study of the product distributions, the pressure dependencies, and the temperature coefficients of the two reactions. The exchange reaction indicated an α-β multiple exchange process occurring, in the mechanism formulated by Anderson and Kemball, between adsorbed phenyl radicals and phenylene bi-radicals. Kemball states "It should be noted that this mechanism does not involve the destruction of the resonance stability of the benzene ring and therefore it is consistent with the fact that the benzene molecule appears to undergo exchange as though it were a saturated molecule". [16] The behaviour of benzene on deuteration is obviously greatly different from that of ethylene and it is interesting to understand how this difference arises. In the case of ethylene exchange and deuteration involve the same type of adsorbed species (ethylene molecules and ethyl radicals) and so

deuteration is often accompanied by a fair amount of exchange which leads to redistribution of the hydrogens. Now, in the case of benzene, exchange occurs through the formation of dissociative species (adsorbed phenyl radicals and phenylene biradicals) but deuteration involves the formation of associative species containing more than six hydrogen atoms and so the two reactions are independent and no redistribution occurs during deuteration."

The suggestion that benzene is chemisorbed as phenyl radicals and phenylene biradicals is supported by Bond,[15] Eley[27] and Burwell.[28] Suhrmann[29] and Gryaznov[30] have reported the evolution of hydrogen when benzene is chemisorbed on nickel, iron and platinum films at room temperature. A dissociative mechanism therefore appears likely, but Kemball has qualified these views in later work on alkyl benzenes.

Crawford and Kemball[31] report the catalytic exchange of many alkyl benzenes on sintered and unsintered nickel films. The aims of the work reported were:-

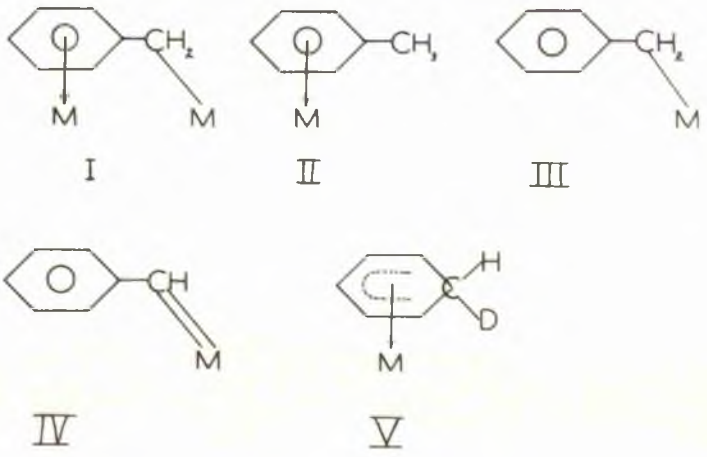
1. To determine the relative reactivities of the hydrogen atoms in the alkyl benzenes to exchange.

2. The effect of sintering the nickel films on their catalytic activity.

Experiments were performed using o-, m-, and p- xylene, toluene, ethyl benzene, cumene and n-propyl benzene. Full discussion of the experimental methods reported in this paper is given below (Section 3). The high reactivity of carbon atoms α to the rings observed on sintered and unsintered films was put down to the lower bond dissociation energies of the carbon hydrogen bonds compared with those for other aryl or aliphatic carbon hydrogen bonds.[1] Roughly similar reactivity is claimed for the α-carbon atoms on sintered and on unsintered films. The effect of sintering is discussed but no positive conclusions are reached. Adsorbed species of types I, II, III and IV are suggested (Figure I). Species I and II are π bonded to the metal while III and

FIGURE I

FIGURE I



IV are sigma bonded through the side chain. The replacement of more than one hydrogen atom for each sojourn on the surface is explained by interconversion of species I and II; species II could exchange only one atom at a time unless conversion to species IV is possible but the authors considered the formation of IV unlikely at low temperatures. The exchange of only one of the methyl groups in cumene during a single adsorption of the molecule on the surface is quoted as evidence for species I. Lower reactivity of ring atoms on sintering is thought to be due to a change in the nature of the catalyst on sintering and relative rate factors of 600 for alkyl group hydrogen exchange and 30,000 for ring hydrogen exchange are quoted as occurring after sintering. Any explanation of the mechanism of the exchange of the ring hydrogen atoms must account for this sintering effect and also a lower reactivity of ortho as opposed to meta and para hydrogen atoms observed on both sintered and unsintered films. Crawford and Kemball also revise the mechanism of the benzene exchange quoted above "because it would not explain why sintering should influence the exchange of the ring atoms more substantially than the exchange of the hydrogen atoms in the saturated side groups." He supports in its place the mechanism favoured by Hartog, Tebben and Zwietering [32] which involves the intermediate known as V (Figure I). An alternative structure, (an adsorbed cyclohexadiene radical), is rejected on the grounds that it involves the loss of the resonance associated with the benzene ring. Structure V uses the five π electrons to bind the species to the metal, the sixth carbon atom having sp^3 hybridisation. The deuterium atom is shown below the plane of the ring suggesting union with a chemisorbed hydrogen atom (Langmuir). The large number of organometallic "sandwich" compounds [33] and the magnetic measurements of Selwood [34] are quoted as corroborative evidence. Garnett and Sollish [35] have also postulated π bonded intermediates in the exchange of halogenated benzenes with heavy water on platinum.

Kemball suggests [31] that special sites are necessary for the formation of π bonded species and that removal of these by sintering explains the drastic effect on the rate of exchange of ring hydrogen atoms.

On the subject of the lower reactivity of the other hydrogen atoms compared with those in meta and para positions Kemball could find no satisfactory explanation. Values of rate constants did not appear to vary with the size of the side group so that steric hindrance was excluded and he quotes Garnett and Sollich [35] who found ortho hydrogen atoms the least reactive in the platinum catalysed exchange of halogenobenzenes with heavy water, but these ortho hydrogen atoms became more reactive with increasing size of halogen substituent. Electronic factors are considered to have some influence on the reactivity of the different positions in the ring although comparison with homogeneous aromatic substitution is obviously difficult. It is known [33] that the inductive and hyper-conjugative effects of methyl substituents strengthen the bond in benzene tricarbonylchromium complexes and a similar effect may be expected for surface intermediates.

Harper and Kemball [36] are on the point of publishing further work on the exchange reactions of alkyl benzenes. The p-xylene deuterium reaction has been studied on films of palladium, platinum and tungsten; reactions which involve exchange as well as deuteration. On palladium at 0°C rapid exchange took place only in the side chain and some of this was multiple exchange (1.69 atoms exchanged per sojourn on the catalyst surface). Ring exchange and deuteration occurred above 20°C. Ring exchange was slow and deuteration was zero order with respect to xylene pressure. Examination of the 1,4 dimethyl cyclohexanes made it clear that exchange occurred during deuteration. No cyclic olefins were observed. On platinum both ring and methyl group hydrogens were exchanged in the temperature range 0-40°C but the former reacted at about one third of the rate of the latter. An increase in the multiplicity (M) of exchange with temperature was noted.

FIGURE II

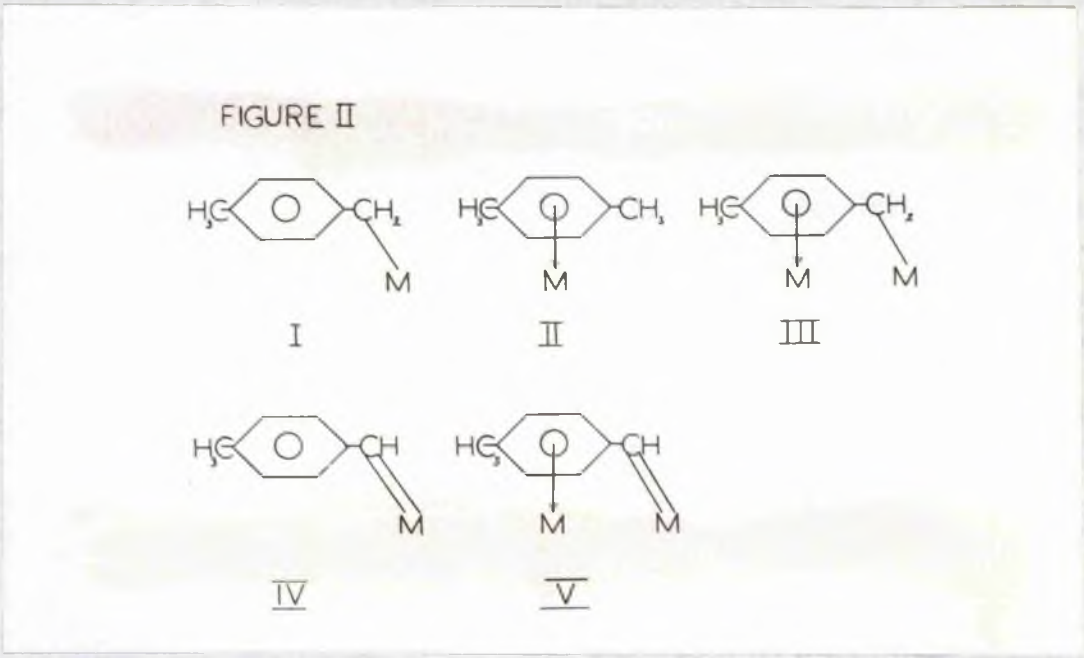


FIGURE II
H3C
CH2
M
I
H3C
CH3
M
II
H3C
CH2
M
M
III
H3C
CH
M
IV
H3C
CH
M
M
V

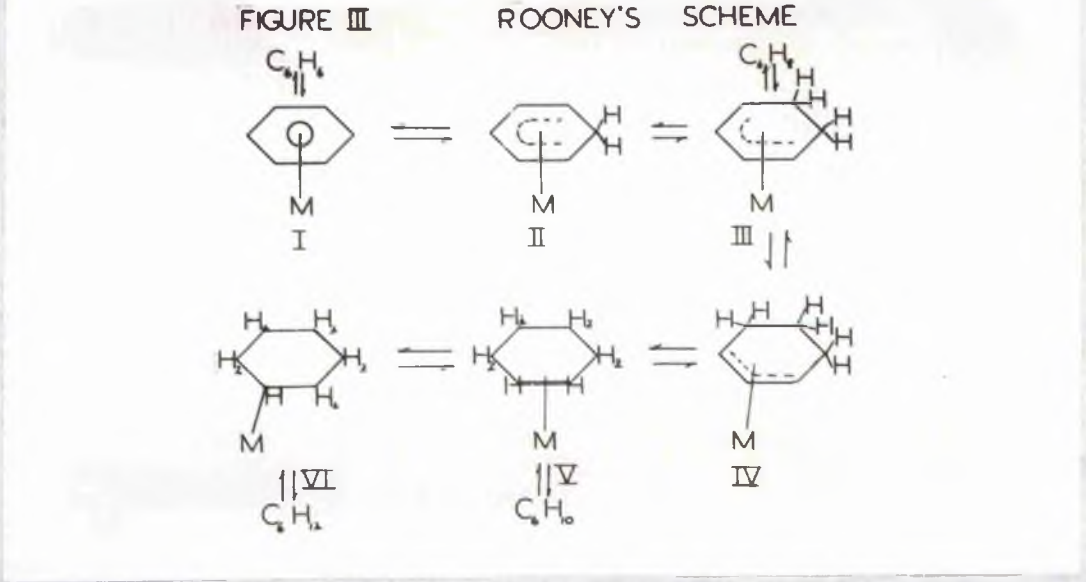
	0°C	20°C	40°C
M_B	1.09	1.64	2.70

As with palladium deuteration occurred in the same temperature range. The ratio of side group exchange on platinum compared with the rate on palladium was 2:15 while deuteration rates were 0.15%/min/10 mg at 52°C on palladium and 9.4% /min/10 mg on platinum at 40°C. Exchange occurred during hydrogenation. Similar results are reported for tungsten.

In discussion the nature of the multiple exchange reaction is considered to be different on each metal. On palladium all six hydrogens in the methyl groups were considered equally likely to be replaced; while on platinum there was a tendency for multiple exchange to occur in the first methyl group attacked, all three hydrogen atoms being replaced. The results on palladium were explained in terms of adsorbed intermediates I, II, and III (Fig. II) analogous with the structures proposed by Crawford and Kemball.[31] On platinum and tungsten two further intermediates are proposed (IV and V Figure II). Interconversion between I and IV or III and V would provide a mechanism for the complete exchange of the methyl group attacked. Crawford and Kemball [31] had objected to structures of types IV and V at these temperatures but they have revised their view on this. Palladium is known [9] to be a poorer catalyst in forming diadsorbed CH_2 from methane and the results were held to indicate that intermediates IV and V were not important for the exchange reaction of p-xylene on palladium.

This paper goes on to survey adsorbed C_6 ring intermediates, extending mechanisms proposed by Rooney.[24] Rooney's scheme is shown in Fig. III and he marshals a body of evidence to support it. The hydrogen

FIGURE III



added may be of either isotopic species. Commenting on this Harper and Kemball [36] make the following points:

1. The shape of the adsorbed intermediates is such that the two groups or atoms attached to an sp^3 hybridised carbon atom will have different orientations with respect to the metal surface. One will be directed towards the surface and one away from the surface.

2. Stepwise interconversion of all intermediates may occur by the gain or loss of the surface directed hydrogen atoms by the Langmuir mechanism.

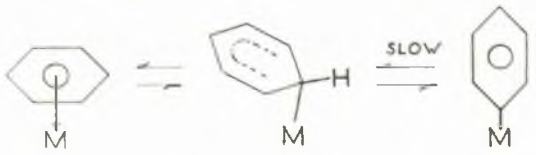
3. Stepwise interconversion of species I to V may occur by an Eley-Rideal mechanism involving the hydrogen atom directed away from the surface.

These mechanisms are used to explain deuteration with and without exchange during the process. They are also a further clarification of the earlier explanation of exchange given by Crawford and Kemball.[31] Relative rates of deuteration and exchange occur because of the relative rates of formation of exchanged I from II compared with formation of III from II. Harper and Kemball consider that this mechanism presents a fuller understanding of the C_6 ring reactions, but although dissociative mechanisms are no longer essential they cannot be entirely discounted. They go on to say that in order to give ring exchange a metal must be capable of catalysing interconversions by a mechanism 3 above (Eley-Rideal mechanism), and if this takes place for C_6X_6 and C_6X_7 (X=D or H) it is likely to occur for other species formed during deuteration as well. This would lead us to expect exchange during deuteration.

The relative rates of ring exchange and deuteration are considered on platinum and palladium and the inference is drawn that reactions essential to ring exchange (interconversion of I and II by Eley-Rideal mechanism) have slightly greater energies of activation than those for

FIGURE IV

FIGURE IV



HORIZONTALLY π BONDED

INCLINED AT +5°

INCLINED AT 90° EDGE-ON σ BONDED

deuteration (interconversion of I and II by Langmuir mechanism). Thus, Harper and Kemball describe deuteration as occurring through a Langmuir mechanism operating through the intermediates outlined above, while exchange occurs by Rideal-Eley mechanism through some of the same intermediates. They add that temperature will affect the amount of interconversion among species I to VI above.

These mechanisms are not the only ones available. Garnett and Sollish [37] report a complex mechanism for catalytic exchange reactions. The results of the exchange of 12 alkylaromatics and of benzotrifluoride with deuterium oxide on activated platinum at 120°C is reported and explained in terms of an associative and dissociative π complex substitution mechanism. The associative mechanism is the same as that used by Crawford and Kemball [31] and first proposed by Hartog et al [32] (Figure I,V). This involves union with a chemisorbed deuterium atom. A mechanism of π-σ bond interconversion is proposed for the dissociative mechanism as shown in Figure IV. The σ bond species goes through a transition complex to a π bonded intermediate. Evidence for the transition state complex and its geometry is provided by comparison with electrophilic aromatic hydrogen exchange.[38] The π complex can revert to the σ bonded intermediate only slowly, and may take up a deuterium atom in the process. The steric effect provided by side groups may then hinder formation of the π complex and the σ bonded radical even when the side group is only a methyl group. This would explain the strong ortho deactivation found. The data from benzotrifluoride indicates that ortho deactivation is not caused by electronic effects of the substituent. The acid catalyzed (liquid phase) exchange which occurs by conventional substitution mechanism (D_3O^+) shows no large steric effect.[39] Hence, "deactivation can only be explained by steric hindrance to the formation of the σ bonded radical in the proposed dissociative mechanism." Randomization reactions between C_6H_6 and

C_6D_6 are equally as fast as the benzene water reaction; this is held to indicate that a dissociative mechanism must be of major importance. Crawford and Kemball [31] considered it important to carry out exchange of the alkyl benzenes with deuterium and not heavy water because the presence of water might have influenced the direction of exchange.

Burwell and Loner [40] report on the exchange between benzene and deuterium at 80°C on chromium oxide gel. No hydrogenation takes place when the gel is activated at low temperatures and exchange is principally simple with some multiple exchange. The exchange of toluene at 110°C occurs ten times faster in the ring than in the side chain. Explanation of the results is in terms of two types of site, one for exchange and one for hydrogenation, depending on the temperature of activation of the gel. The authors "somewhat favour" a dissociative process as a mechanism to explain the reaction.

Hiroto and Ueda [41] have published work on the exchange of para-xylene with deuterium oxide at 100°C. In one series it was found that

1. Platinum and palladium exchanged methyl and ring hydrogen atoms.
2. Iridium, ruthenium and rhodium exchanged them less readily.
3. Cobalt and nickel exchanged only methyl hydrogens.
4. Silver and copper could not exchange either type of hydrogen.

Easier exchangibility of the methyl hydrogens was explained in terms of carbon hydrogen bond strengths, [48] and formation of an adsorbed benzyl radical.

A "selectivity ratio" (degree of ring hydrogen exchange to methyl hydrogen exchange) gives an order of metal activity based on this ratio as:

Pt > Pd > Cr > Ru > Rh > αCo, βCo, > Ni

This is said to show a relationship with the nearest atomic distances of the metals in their crystals. Exchange of ring hydrogens is explained in

terms of adsorbed dimethylcyclohexadiene diradicals and p-xylyl radicals. The metal reactivities of platinum and nickel are explained in terms of lattice geometry.

Summary

The deuterium hydrocarbon reactions for benzene and various alkyl benzenes, particularly p-xylene have been investigated on metal films of nickel, iron, silver, palladium, platinum and tungsten. In most cases exchange is accompanied by varying amounts of deuteration. Exchange in the side chains always seems to occur faster than in the ring, consistent with the observed carbon-hydrogen bond strengths. Simple and multiple exchange occurs. Various mechanisms have been put forward, the most recent involving π bonded (associative) and the earlier involving σ bonded (dissociative) intermediates.

Reactions between alkyl benzenes and heavy water and halogenobenzenes and heavy water on activated platinum catalysts, and alkyl benzenes and deuterium on chromium oxide gel also occur and some similarity with reactions on metal films has been suggested although this view is disputed.

If reactions on thin film only are considered it can be seen that Kemball began by explaining the reactions of benzene with deuterium as two separate, unconnected processes. The conventional α-β process could be used to explain exchange and some evidence for dissociative adsorption is seen to be available. In trying to relate ring exchange and the deuteration reaction Kemball has been forced to adopt an associative adsorption and a complicated dual mechanism. It would appear that a reversion to conventional ideas of dissociative chemisorption - perhaps on the lines suggested by Garnett and Sollich's mechanism - and separation of the deuteration process from the exchange would simplify the existing picture of the reacting system. It would appear from the published temperatures at which reaction occurred, summarised below,

that it would be possible for the adsorbed dimethylcyclohexane to undergo exchange after deuteration but before desorption. This would explain the results obtained by Harper and Kemball where exchange is shown to have occurred during deuteration, and avoid the necessity of involving an Eley-Rideal mechanism to explain exchange occurring at the same time as a Langmuir-Hinchelwood mechanism explains hydrogenation.

Section 1.2 h

Summary of metal activities

TABLE I

Comparison of temperatures at which rates have been measured on different metal films for:-

1) Exchange

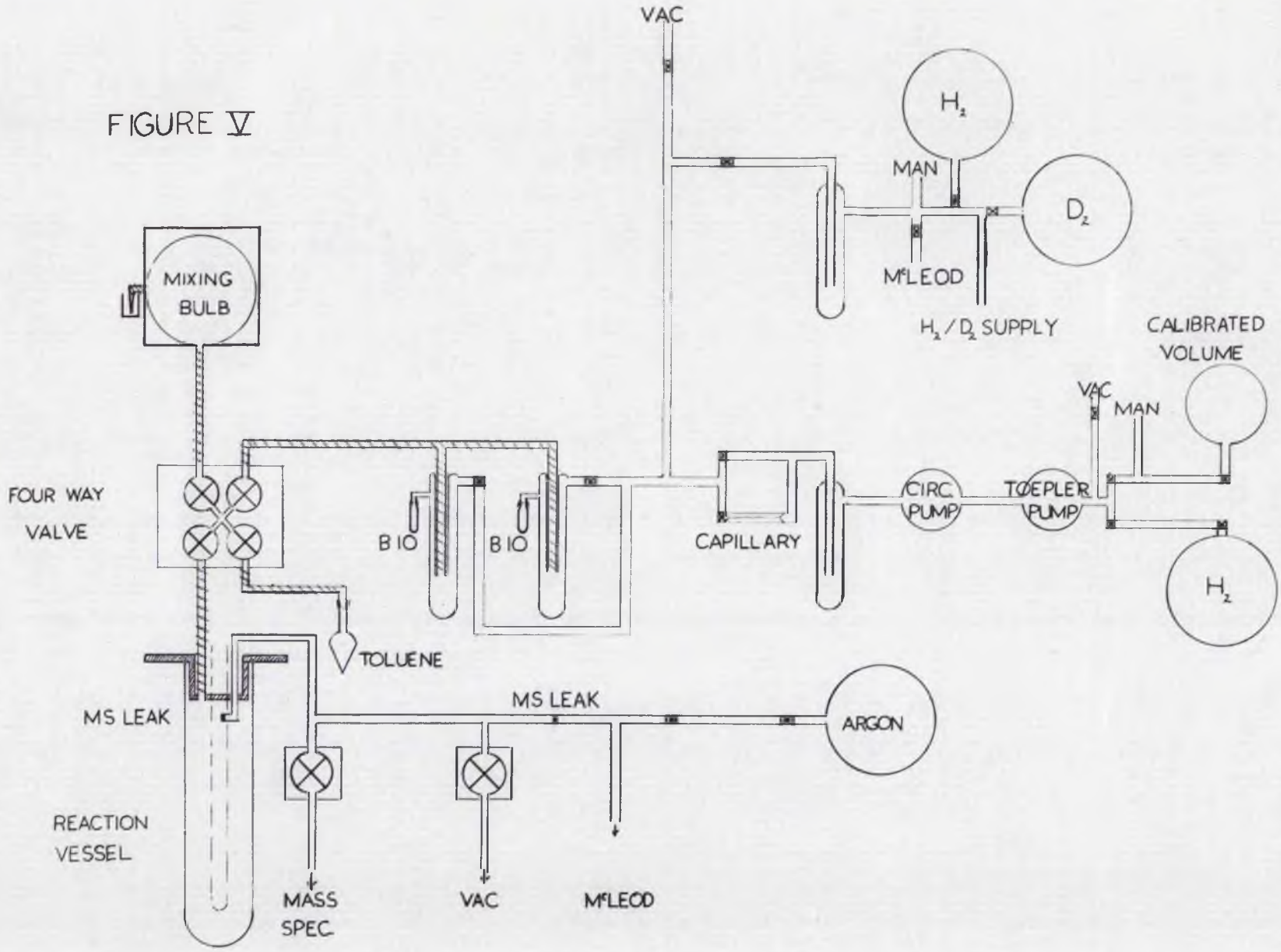
Hydrocarbon:-	Methane	Ethane	Cyclohexane	Benzene	Toluene	p-Xylene	
Nickel	206-255°	162-195	-35-0°	Too fast at -45°	-10°	-10°	°C
Palladium	243-308°	145-207°	18-82°	0-58°	-	0-76°	"
Platinum	159-275°	134-192°	0-31°	-22.5°-43.5°	-	0-40°	"
Iron	Inactive	Inactive	-	Too fast at 0°	-	-	"
References	8,9	12	21	26	31	36	

2) Hydrogenation

Hydrocarbon:-	Benzene	Toluene	p-Xylene	
Nickel	23-58°	45°	-	°C
Palladium	0-58°	-	20-110°	"
Platinum	-22.5° to 43.5°	-	0-40°	"
Iron	23-58°	23°	-	"
References	31	66	36	

This table represents a summary of the results discussed above, but must be treated with caution as conditions varied from one series of experiments to another. This is particularly true of the hydrogenation reaction where ratios of reactants were not the same.

FIGURE V


VAC
H₂
MAN
D₂
McLEOD
H₂ / D₂ SUPPLY
CALIBRATED VOLUME
VAC
MAN
MIXING BULB
FOUR WAY VALVE
B I O
B I O
CAPILLARY
CIRC. PUMP
TOEPLER PUMP
H₂
TOLUENE
MS LEAK
MS LEAK
ARGON
REACTION VESSEL
MASS SPEC.
VAC
McLEOD

Section 2. 1

Description of General Apparatus

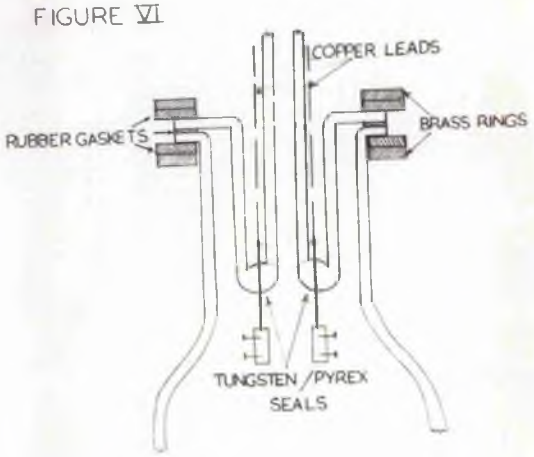
See Figure V.

The general features required in the apparatus were a reaction vessel which should be demountable and contain a pumping lead, two electrical leads to the wire to be evaporated and later, a mass-spectrometer leak. The reaction vessel had also to be of minimum volume and to be capable of being heated to 400°C. for two hours. In order to operate a useful experimental sequence this reaction vessel was designed with a connection to a system of four valves, one to the reaction vessel, the second to the mixing bulb, the third to the toluene supply, and the fourth to the pumping system. The lead to the pumping system then passed through two liquid air traps in parallel. These traps and the whole apparatus above described were wound with heating tape to make it possible to remove toluene to the traps. From the traps to the reaction vessel no vacuum grease was permissible, firstly because of the solution of toluene in such grease and the possibility of loss of exchanged toluene, and secondly because of the deleterious effect of tap grease on metal film catalysts. (Ashmore, Wright, and Kemball).[10]

The liquid air traps then led to B10 cones into which the reacted toluene could be distilled and removed for I.R. analysis. The reacted hydrogen was taken through a capillary lead to avoid carrying over toluene and could be pumped by a separate system into a calibrated volume to find the final pressure of hydrogen in the reaction mixture. The hydrogen was supplied from a five litre bulb via a manometer and liquid air trap. A Pirani gauge could be used to replace the manometer in the 1-10 mm. pressure range. A conventional liquid air trap, mercury diffusion pump and rotary

FIGURE VI

FIGURE VI



FIRST REACTION VESSEL

oil pump were used to maintain the vacuum. A low pressure Pirani gauge was also connected to the apparatus to check the pressure during evaporation and for normal use.

(a) Development of the reaction vessel and valve system

The reaction vessel and four valve system presented problems of design which were overcome in the following ways.

The original reaction vessel consisted of a glass vessel, (see Figure VI), with the end flared out into a flange. This was sealed to a matching glass flange with a Cenco rubber gasket and the flanges held together by steel bolts acting on rings above and below the flanges. The electrical connections to the wire to be evaporated were through tungsten-glass seals. This vessel was connected to a four valve system of glass bodied valves operated by screws acting on Cenco rubber diaphragms.

This apparatus was discarded when it was found that the toluene was discoloured by the Cenco rubber in the valve diaphragms and heating the reaction vessel walls heated the Cenco gasket, leading to a rise in pressure and possible poisoning of the catalyst. The tungsten glass seals were suspected of leaking at high current as this also led to a rise in pressure. The reaction vessel was replaced by a second design, (see Figure VII), which sealed a ground glass flange to a mild steel flange with an indium wire gasket. The indium wire seal was made by pressing the 1 mm. diam. wire lightly between the metal and glass flanges and then evacuating the reaction vessel. The seal was entirely satisfactory in operation. The glass flange was held to the metal flange by bolts passing through a ring. Provision was made for cooling the metal flange with a water stream through a copper tube in the flange. The electrical leads were made through Nilo K wires sealed into the ends of small Nilo K tubes with C40 grade glass which provided insulation as well as vacuum tight sealing. These Nilo K

FIGURE VII

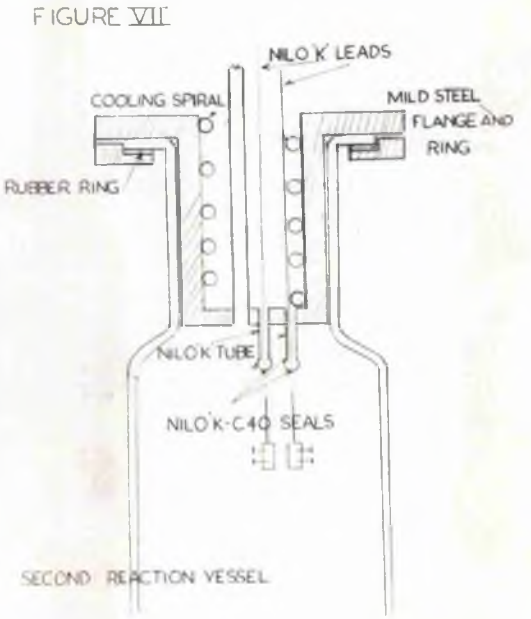
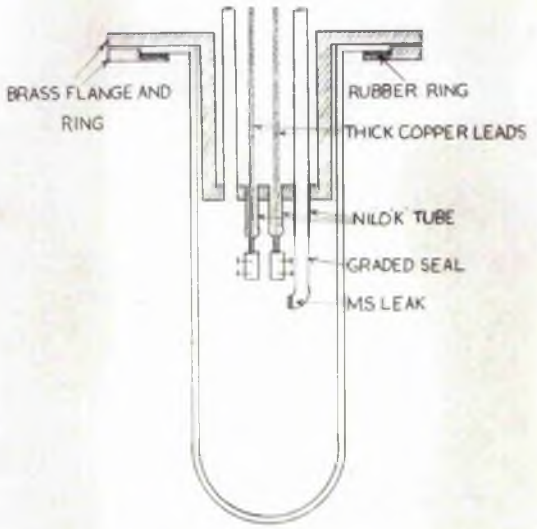


FIGURE VII
NILO K LEADS
COOLING SPIRAL
MILD STEEL
FLANGE AND
RING
RUBBER RING
NILO K TUBE
NILO K-C40 SEALS
SECOND REACTION VESSEL

FIGURE VIII

FIGURE VIII



FINAL FORM OF REACTION VESSEL

tubes were fixed to the metal flange with silver solder. In operation it was found that heating the reaction vessel to 400°C. caused the zinc to distil from the silver solder and leaks to develop slowly in the reaction vessel. The water cooling of the flange was not found to help this difficulty and the resistance of the Nilo K wires caused excessive heating and cracking of the C40 glass seals. Provision of a mass-spectrometer leak was also difficult due to the flange size. The design was modified to reaction vessels of larger size and with a large brass flange, see Figure VIII, incorporating a wide pumping lead. The thick copper electrical leads were soldered into brass ends to small Nilo K tubes. These tubes were connected by C40 glass seals to larger Nilo K tubes which were soldered into the brass flange. A mass spectrometer leak was fitted and turned upward to prevent blocking with evaporated metal from the filament. The reaction vessel was sealed to the brass flange with an indium wire seal. The soldered joints were arranged to be high enough above the heated area to avoid the earlier distillation problem. Use was also made of copper electrical leads which were of robust size and acted as heat sinks. The larger brass flange made a wider pumping lead possible and easier distribution of the electrical and mass spectrometer leads. It also acted as a large heat sink and reduced the effect of the heating gun on the leads attached to the flange.

The four valve system was replaced by a stainless steel valve involving sealing by pushing a soft copper cone against the hard steel seating. The cone moved on a Monel metal diaphragm sealed to the body of the valve with soft aluminium gaskets. (see photograph Figure IX and photograph Figure X.) This exactly fulfilled the conditions required, i.e. a greaseless valve system incapable of poisoning the catalyst. The design of this valve has already been described. (Rhind).[43]

FIGURE IX

FIGURE X

(b) Volume of the reaction vessel etc.

The volume of the reaction vessel used was 489 ml. except for one experiment carried out in a reaction vessel of 266 ml. to find if volume has an effect on reaction rate. The volume of the mixing bulb was 168 ml. These volumes, which included lead tubes, were measured by expansion from a calibrated volume used to measure the final hydrogen pressure. The reaction mixture was made up by allowing a known vapour pressure of toluene to fill the mixing bulb and freezing this quantity down into a small tube attached to the bulb. Hydrogen was then admitted and its pressure controlled to the required value. It was found that the size of the small tube containing the frozen toluene at 90°K affected the hydrogen pressure and the tube was modified until this effect was negligible.

The reaction vessel temperature could be controlled by immersion in a large dewar vessel fitted with a lid, a stirrer, a heater, and a temperature controlling device. The dewar vessel was filled with water or oil depending on the temperature required. The control device was a bi-metallic strip claimed to be sensitive to ± 0.1°C. For temperatures of 0°C. an ice and water bath was used.

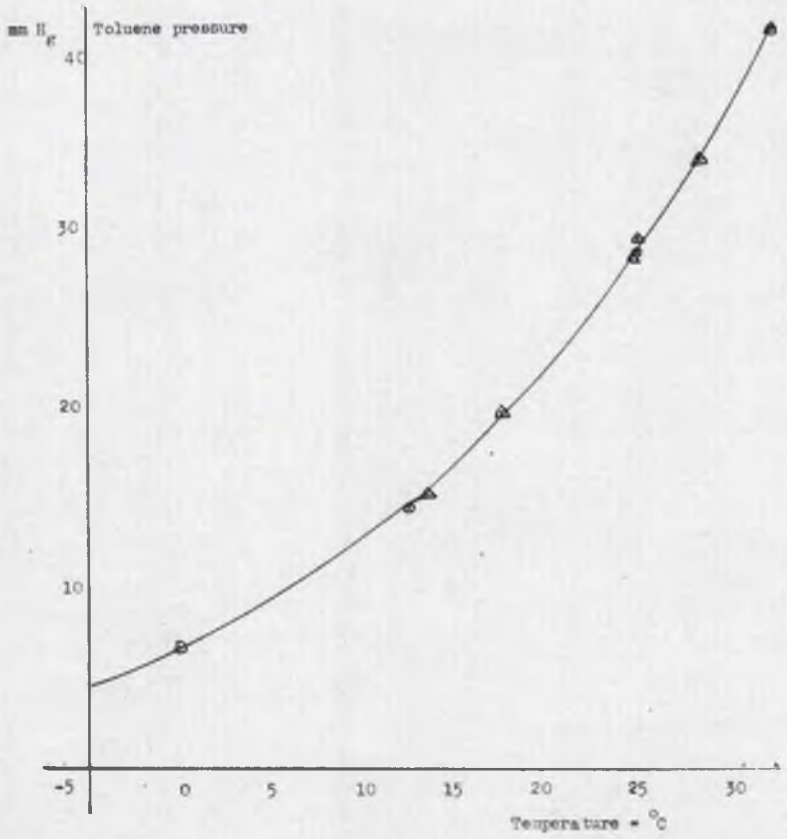
(c) The toluene supply

The toluene supply temperature could be controlled by a similar bath. The vapour pressure of toluene has been reported by a series of authors in the region of interest. The most recent is the work of Pitzer and Scott.[44] These authors derive the equation

$$\log_{10} p = \frac{2666.52}{T} + 6.7 \log_{10} T + 27.6470$$

and from this the pressure at various temperatures can be calculated and a graph drawn of the region 261°K to 281°K. (see Figure XI.)

FIG XI



VAPOUR PRESSURE OF TOLUENE

⊙ Pitzer and Scott

△ Schmidt

T.°K	264	265	267	269	271	273	275	277	279
p. mm.	3.42	3.93	4.50	5.14	5.86	6.75	7.59	8.58	9.71

Pitzer and Scott claim good agreement with International Critical tables III, 213.

Section E. 2.

Preparation and purification of materials

(1) Deuterium

Deuterium was prepared by reaction of D_2O with metallic zinc at about 400°C.. The method is described in Kirschenbaum; Physical properties and Analysis of Heavy water.[45] It is attributed to Johnston, 1943.[46]

The apparatus consisted of a heavy water reservoir connected to a tube filled with granulated zinc which could be heated to 400°C.. It was not heated to more than 419°C., the melting point of zinc. This furnace then led to a liquid air trap through a tap. Between the tap and the trap a second inlet was available for the introduction of cylinder hydrogen for purification through the liquid air trap and the heated palladium thimble which followed the trap. The purified hydrogen or deuterium, was collected with a Toepler pump and stored in a 5 litre reservoir. The heavy water used was 99.78 D_2O. The heavy water was supplied in a sealed ampoule and broken under vacuum. The water was then distilled into the reservoir out of contact with ordinary water. Before preparation of deuterium, the heavy water was thoroughly freed from gas and the furnace heated to about 400°C. to remove any ordinary water on the zinc. The apparatus was then shut off from the pumps and the D_2O allowed to distil into the region of the hot zinc. The D_2O reservoir was at room temperature.

When a pressure of deuterium was obtained the palladium thimble heater was switched on and the thimble allowed to warm up slowly.

The early gas samples were rejected in case ordinary hydrogen had remained in the palladium thimble and the remaining gas collected and pumped into the reservoir. About 20 mm. of D_2 was collected in a 5 litre bulb in about 8 hours. The rate of production depended on the palladium thimble temperature. Checks on the deuterium/hydrogen ratio were made using the mass spectrometer and the gas usually proved to be about 99.5% D.

(2) Toluene

Reagent grade toluene was purified by the following process.

1. Shaken with conc. H_2SO (10% by volume) a minimum of ten times or until the sulphuric acid layer was colourless.

2. Shaken with successive lots of NaOH solution.

3. Shaken with successive lots of water until the water layer was neutral.

4. Distilled from P_2O_5.

5. Dried with metallic sodium.

6. Distilled in a fractionating still with a reflux ratio of 2/25 when the thermometer was steady at 110°C.

7. Infra red spectrum of the resulting material recorded and compared with the spectra in A.P.I. Tables No. 308.

(3) Wires

Nickel, tungsten and palladium wires were obtained from Johnson, Matthey and Co. Ltd. in the highest purity obtainable and used without further purification. Iron wire of grade II was used.

Section 2, 3

Description of experimental method

The procedure for an experiment involved the following routine.

1. The wire filament was weighed.

2. The wire filament was fitted into its holders in the reaction vessel, and the reaction vessel sealed into place with a fresh indium wire seal and pumped out.

3. The electronic equipment of the mass spectrometer was switched on and the background pressure of the spectrometer checked. When the pressure was sufficiently low the mass spectrometer filament was switched on using a high value of the electron accelerating volts.

4. When the reaction vessel and the general apparatus had been pumped out to less than 10^{-5} mms. the heating can was switched on round the reaction vessel and the wire to be evaporated was slowly heated to free it from gas.

5. The toluene supply was thoroughly freed from gas and the required pressure of toluene admitted to the mixing bulb, the temperature of the bulb being noted.

6. The toluene in the mixing bulb was frozen down in liquid air in the small tube attached to the mixing bulb, and the required pressure of deuterium admitted.

7. The mixing bulb was sealed off and the liquid air removed. The small tube then warmed up and the toluene and deuterium were mixed for at least one hour.

8. The heating can took one hour to reach 400°C. and was maintained at this temperature for a further 2 hours. The wire to be evaporated was gradually warmed by increasing the current until it was just below the evaporating temperature and was kept at this temperature for one hour or until the pressure was less than 10^{-5} mms.

9. When removal of gas from the wire was complete (pressure $< 10^{-5}$ mm.) the wire temperature was reduced, the heating can removed and the reaction vessel allowed to cool.

10. A dewar vessel containing ice and water was put around the reaction vessel and the current in the wire slowly raised until evaporation occurred.

11. When a sufficiently thick film had been prepared the current was reduced and switched off and the dewar vessel temperature arranged to be that required for the reaction.

12. The electron volts were reduced on the mass spectrometer and the instrument allowed time to become steady. The valve connecting the mass spectrometer was opened and the pumping load closed so that the reaction vessel was connected directly to the mass spectrometer. A scan of the background was taken to ensure that impurities were not present.

13. The reaction mixture was admitted to the catalyst and the time noted. The excess of the mixture, which remained in the mixing bulb, was pumped away. Scans of the mixture of toluenes were obtained at noted times. After about two hours,(the longest period permissible without pumping away an appreciable part of the reaction mixture) the electron volts were raised, the toluenes scanned with Hg^{++} as a mass marker and the heights of the 2^+, 3^+, and 4^+ peaks were determined.

14. The mass spectrometer was shut off from the reaction vessel and switched off when convenient. The reaction mixture was let out of the reaction vessel and pumped through the liquid air traps. If required the pressure of the remaining hydrogen was measured. The toluene remaining in the liquid air traps was distilled into a receiver, removed and the infra-red spectrum recorded in CS_2 solution.

15. The reaction vessel was dismantled and cleaned. The filament was reweighed.

Section 2.4

The preparation of evaporated metal films

Beeck et al [48] described the procedure necessary to prepare evaporated metal films which were reproducible and of high catalytic activity. Stress was placed on the necessity to bake out the reaction vessel surface at 500°C. for two hours prior to the deposition of the film. The occluded gas in the metal filaments had also to be removed and this was done by heating the filament electrically to just below the evaporation point for the final hour of the baking out process. The reaction vessel had to be allowed to cool and the vessel wall kept at the correct temperature during evaporation. It was shown that the activity of the film was reduced by increased wall temperature during evaporation. Evidence of the structure of the films using X-ray diffraction and electrical conductivity measurements was obtained. The activity of the films was measured by the rate of hydrogenation of ethylene.

Precise details of wire measurements and evaporation currents were supplied by Kemball.[49] This author suggests de-gassing of the glass surface at 450-500°C. for two hours with the metal filament at just below evaporation temperature for the last 30 minutes. The glass surface was maintained in ice during evaporation, except for copper which was evaporated in an acetone-CO_2 bath. The weight of film was found by weighing the filament before and after evaporation. Recommended sizes were given, with the appropriate degassing and evaporating currents. His data are copied out below.

Platinum Very fine wire round 0.25 mm tungsten wire (5.4, 5.8 amps. or greater).

Palladium 0.2 mm. wire wound around 0.3 mm. tungsten wire (2.6 A, 6.8 A)

Nickel 0.5 mm. wire was used (4.7 A, 4.2 A)

Iron Two strands of 0.2 mm. wire twisted together. (1.1 A, 3.2 A)

Copper Pieces of rolled copper suspended in a coil of 0.3 mm. tungsten wire.

Kemball claimed that the catalytic activity of the films of platinum, palladium, nickel and iron, was proportional to the weights of the films. Extensive evidence was offered concerning surface areas of films and their structure determined by electron diffraction. These films were used to catalyse the exchange of deuterium with ammonia.

In a later paper Crawford and Kemball [31] offered further details of the preparation of nickel films used for the exchange reaction between toluene and deuterium. One change in the procedure was noted, the nickel filament was cleaned by flashing in pure hydrogen before the vessel was degassed.

The method used for the experiment reported here followed substantially the method used by Kemball. Films of nickel were the first to be prepared. Early experiments omitted the glass degassing stage and relied on torching the glass with a gas-air flame. These catalysts were completely ineffective judged by their ability to equilibrate mixtures of hydrogen and deuterium. The provision of a heating coil which reached 450°C. in one hour and remained at that temperature when first constructed, made it possible to prepare films which converted H_2 and D_2 mixtures to the theoretical equilibrium mixture in a very short time. Theoretical values have been calculated by Urey and Rittenberg.[50] Difficulties then arose in the design of a suitable reaction vessel. These are discussed above. They were overcome satisfactorily and films were prepared in routine fashion without difficulty.

Nickel and Iron were used as wires, while platinum, palladium

and copper, were used as wires wound on supporting tungsten wires. Holland [51] quotes melting points and evaporation temperatures equivalent to the temperature at which the vapour pressure is 10 microns Hg. (Dushman)[52]

Metal	Melting Pt. °C	Evap. Temp. °C	Interaction with Tungsten
Iron	1535	1447	Alloys with tungsten
Nickel	1455	1510	" " "
Platinum	1774	2090	Partial alloy with tungsten
Palladium	1555	1566	
Copper	1083	1273	Does not readily wet tungsten

In this investigation it was found that platinum, palladium and copper wires broke before evaporation began. Nickel was usually very easily evaporated from a wire. The iron wires broke close to the barrel connectors during evaporation when used a second time. In case this had been due to handling the wires were handled with tweezers but the same difficulty occurred. The tungsten wire used as a support sometimes broke during evaporation especially in the case of platinum films. The time involved in degassing the glass and other preparations, was wasted and since further experimentation could not occur on any day when a wire broke during the evaporation, strong efforts were made to ensure that wires did not break during evaporation. The routine used in filament preparation and evaporation was :-

1. Nickel films

25 cm. of 0.5 mm. nickel wire were removed from the supply spool with pliers and the cut length doubled into a hairpin. The ends fastened to the barrel connectors were doubled to increase the area of contact. The filament was cleaned with CCl_4, dried and

weighed. It was then screwed into the barrel connectors and rinsed with CCl_4. The reaction vessel was then mounted in place and evacuated. While the glass was being degassed the filament was degassed by slowly raising the current until it was a bright orange colour in the hot vessel. The current necessary was usually 5 A. After degassing, the pressure being less than 10^{-5} mm. the filament and reaction vessel were allowed to cool. The reaction vessel was then surrounded by a dewar vessel filled with ice and water and evaporation of the filament carried out with a current of about 5.8 A. After reaction the reaction vessel was cleaned with aqua regia, water and "Teepol" and finally with distilled water, dried and was then ready to be replaced. Occasionally the reaction vessel was cleaned with chromic acid.

2. Iron films

50 cms. of 0.2 mm. iron wire were removed from the spool (kept in a desiccator) and twisted together avoiding touching the wire where possible. The procedure was then the same as that used for nickel except that degassing was carried out at 1.6 A and evaporation between 2.2 and 2.4 A.

3. Palladium and Platinum films

The wire to be evaporated was wound by hand on a tight helix on 25 cms. of tungsten supporting wire. The tungsten was shaped before winding into a suitable hairpin. The completed filament was washed with CCl_4 and the evaporation procedure followed was similar to that followed in the case of nickel. Degassing and evaporating currents depended upon the diameter of the tungsten supporting wire. If this support wire was too thick the current required was very high and this was avoided, where possible, to prevent the conduction of heat back up the electrical leads with consequent damage to the vacuum seals. When the support wire was too thin the filament became very fragile during its first use

(the tungsten wire tending to shatter) with consequent wastage of valuable metal wire.

Platinum

With 36 s.w.g. wire wound around 0.3 mm. tungsten the tungsten broke at 9 A without evaporation. 36 s.w.g. wire wound on 0.25 mm. tungsten produced a film at a current of 6 A. This filament broke on removal from the reaction vessel. A robust filament was made by twisting together two strands of 36 s.w.g. platinum wire with two strands of 0.25 mm. tungsten wire. This required an evaporating current of 10 A.

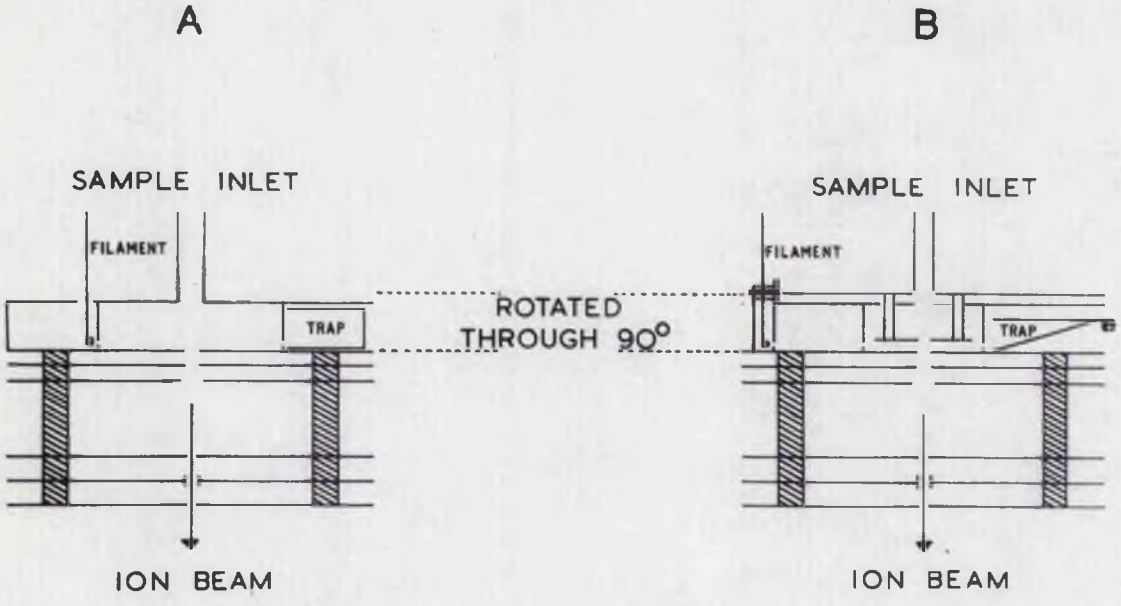
Palladium

0.2 mm. palladium wire was wound around 25 cms. of 0.3 mm. tungsten wire. These filaments were degassed at 4.5 A and evaporated at 7.0 A. The tungsten wire became very brittle and not more than three evaporations were possible from one filament. These films were relatively simple to evaporate.

4. Copper

0.2 mm. copper wire was wound on 25 cms. of 0.3 mm. tungsten wire. Heating the tungsten wire to evaporate the copper caused the copper to form a drop which was pulled up the wire attached to the unmelted copper. When all the copper melted, the drop ran back down the hot wire producing a film. This film was ineffective at 0 and 20°C for the reaction studied. It was, however, prepared in an ice water bath and there is evidence that the film would sinter at this temperature (Allen and Mitchell).[3]

FIG. XII


A
B
SAMPLE INLET
FILAMENT
TRAP
ROTATED
THROUGH 90°
SAMPLE INLET
FILAMENT
TRAP
ION BEAM
ION BEAM

Section 2. 5

THE MASS SPECTROMETER

Description

The reaction mixture was analysed in a conventional 60° sector field Nier type mass spectrometer.

This instrument was equipped with the usual stabilised H.T. and magnet current supplies. The magnet current was varied at constant H.T. (1840 volts) to focus the ion beam on the collecting electrode. The magnet current could be scanned manually or electrically. The signal was amplified by a 100% feedback amplifier and the signal displayed on a moving chart recorder.

The entrant gas was ionised by a stream of electrons from a hot filament, the temperature of the filament being controlled by a circuit which ensured a constant trap current. See Figure XII. It was also possible to vary the voltage accelerating these ionising electrons. The electrons were constrained in tight helices by the presence of a magnetic field acting in the same direction as the electron flow. The strength of this field was important and is discussed below.

The reaction mixture was sampled through a slightly porous leak and passed from the reaction vessel to the mass spectrometer room by a long glass tube of 25 mm. O.D., about 10 metres long.

Although the build-up to equilibrium was noticeable, it occurred within five minutes of the mixture first reaching the leak and is therefore not considered to have affected the distribution of the toluenes in the analysed mixture.

Instrument resolution

The instrument had to be set up to provide a resolution of 1 in 200 even at low electron accelerating volts, and had also

to be able to analyse hydrogen-deuterium mixtures at higher electron accelerating volts. This was found to be difficult for two reasons. Firstly, the magnet field applied to the electron beam could also remove hydrogen ions or make it very difficult to focus them in sufficient numbers to give reasonable sensitivity. Secondly, the system was found to pump hydrogen very inefficiently. It was found possible to provide reasonable resolution together with sensitivity to hydrogen if a value of 180-200 gauss. was used for the strength of the field applied to the ion beam. At higher values, sensitivity to hydrogen decreased, while at lower values the resolution fell below the target figure 1 in 200.

The difficulty with pumping hydrogen has already been noted by Bleaney and Hill.[54] The problem was that while the argon peak was steady the hydrogen peak varied as much as 10%, apparently because of irregular boiling and back diffusion. The mercury pump used was rated at mains voltage (240 v. AC.), and Bleaney and Hill suggest increasing the power supplied to maintain the designed pumping speed. This was found to increase the variation of the peak and it was found that reduction of the supply voltage to 208 volts gave very smooth running. The makers advised cleaning the pump and buffing the inside to a high polish. This also was done and an improvement again noted. The inclusion of steel wool or stainless steel meshes to make the mercury boil regularly was not found to have a helpful effect. The above improvements did not affect adversely the steadiness of the argon peak. It is assumed that under the conditions of use to which the pump is put the makers rating is too high for stable pumping at a low throughput of gas. The instrument resolution was improved by lining up the tube in the magnet and by adjustment of magnet and ion-gun electrode controls until the mercury peaks

from mass 99 to mass 102 (Eg. doubly ionised) could be substantially resolved. In addition the repeller plate had to be maintained at box potential and the resolution was checked at lower electron accelerating volts to ensure that the resolution did not deteriorate as the electron volts were reduced.

Sensitivity

The sensitivity of the instrument was very high at high electron volts but fell rapidly as the voltage was reduced. At the voltage used it was usually 1 volt per millimetre of toluene applied to the reaction vessel leak. Hydrogen - deuterium ratios were measured at higher electron volts and sensitivity was an embarrassment more than a problem as the value of the grid leak resistance had been raised to 4×10^{11} ohms to increase sensitivity. The hydrogen - deuterium sensitivity was arranged to be about 1 volt per millimetre applied to the reaction vessel leak at 45 E.V. and using the lower grid leak resistance of 2×10^{11} ohms.

Memory Effects

No memory effects was recorded although checks were made from time to time on the background in the mass spectrometer. The mass spectrometer tube was permanently heated to avoid this difficulty and the ion gun assembly was heated by running the filament for some time before measurements were taken.

Sampling leak

The sampling leak used was the Metronil porous clay type which seals into pyrex glass. Its porosity had to be carefully controlled so that the amount of toluene reaching the mass spectrometer would be sufficient to give reasonable sensitivity while the faster diffusing hydrogen mixture did not leak away rapidly enough to affect the reaction mixture composition.

A leak was constructed and heated until it was of such low porosity that it satisfied the above conditions.

Diffusional errors due to hydrogen diffusing faster than deuterium were estimated by putting known mixtures on to the reaction vessel leak. The ratio of hydrogen to deuterium was, however, only used as a check on the extent of reaction. It was assumed throughout the calculations that the sensitivity of the instrument to deuterium containing toluenes remained the same as the sensitivity to normal toluene.

The Mass spectrum of toluene

The major feature of the mass spectrum of toluene at high electron volts is the series of three peaks at m/e 91, 92, and 93. Their relative intensities were reported variously as

	A.P.I. 176		A.P.I. 251	
m/e	50 E.V.	70 E.V.	50 E.V.	70 E.V.
91	100	100	100	100
92	77.8	75.6	79.3	77.0
93	5.54	5.24	5.6	5.44

A.P.I. 305

m/e	50 E.V.	70 E.V.
91	100	100
92	79.24	78.5
93	5.06	5.6

The appearance potential for $C_7H_7^+$ (mass 91) was quoted as 11.8 E.V. by Schissler et al[55] while that of $C_7H_8^+$ (mass 92) was reported as 8.7, 9.15 and 9.23 E.V. (Morrison et al 1952,[56] Nief 1951,[57] Omaru et al 1955)[58]. As is to be expected it is possible to remove the 91^+ peak and thus simplify the spectrum by reducing the electron volts. If the variations in the above reported values were due to instrumental differences it appeared necessary to find how the spectrum on our instrument varied as the accelerating voltage was reduced. The changes are shown in Figures XIII and XIV.

The ionisation efficiency curve Figure XIII shows the drop in sensitivity. This was the same for the 92^+ and 93^+ peaks while the 91^+ peak vanished at an indicated voltage of 14 E.V. The relative peak height curve Figure XIV removes this change in sensitivity and it is seen that the 92^+ and 93^+ peaks maintain the same relative sensitivity while the 91^+ peak vanishes at 14 E.V.

Kendall [31] discusses this method of analysing toluene and reports that at 14 E.V. 35% fragmentation of toluene occurred. It is assumed that this was due to instrumental differences. It is certainly true that variation of the repeller electrode on the instrument used caused an appearance of the 91^+ peak and it was for this reason that the electrode was maintained at box potential. The 91^+ peak was said to vanish when it was no longer discernible in the background noise of the amplifier. This meant the peak was always less than 0.1% of the highest peak in the spectrum. It was possible to check the absence of the 91^+ peak and also the relative intensities of the 92^+ and 93^+ peaks at the operating voltage of 13 E.V. when catalysts failed to be effective. These checks never showed the 91^+ peak to have reappeared and maintained the ratio of 92^+ to 93^+ as 100:6. The reaction was followed by

scanning the 90-101 m/e region electrically, peaks being observed at m/e 93-101 corresponding to species having exchanged 1 hydrogen atom to 8 hydrogen atoms (referred to as d_1 to d_8).

Calculation of deuterium distribution in the toluenes

Calculation of percentages of exchanged toluenes was possible by the use of the ratio found for 92^+ to 93^+ (100:6). The 92^+ peak arises from the parent molecule singly ionised and the 93^+ peak from natural ^{13}C and deuterium in normal toluene. It was assumed that the sensitivity of the instrument remained the same to toluene containing deuterium and that the same ratio was maintained. The individual scans were converted into percentages of toluene d_0, toluene d_1 etc. by the formulae

d_0 = 100% of 92^+ peak + 6% of 92^+ peak

d_1 = (93^+peak - 6% of 92^+peak) + 6% of (93^+peak - 6% of 92^+peak)

d_2 = [(94^+peak - 6% of (93^+peak - 6% of 92^+peak)] + 6% of [

and so on.

$$\% d_0 = \frac{d_0}{92^+ + 93^+ + 94^+ \text{ etc. peaks}}$$

In words this is adding 6% of the peak height of 92^+ to 92^+ and subtracting this from 93^+. 6% of the resulting figure was then added to it and subtracted from 94^+ and so on. The percentage of one species was then calculated from the total of all peaks measured on a scan. Percentages were estimated to the nearest 1/2%. At the end of the experiment the hydrogen-deuterium ratio was determined at 45 E.V. and a scan of the final mixture of toluenes recorded. At this

electron voltage Hg^{++} peaks appeared making it possible to label the toluene peaks with their appropriate masses.

The hydrogen - deuterium ratio was determined by finding the 2^+, 3^+, and 4^+ peak heights and applying the formula.[59]

$$\text{Proportion of atoms of deuterium } p = \frac{[HD] + 2[DD]}{2([HH] + [HD] + [DD])}$$

FIGURE XIII

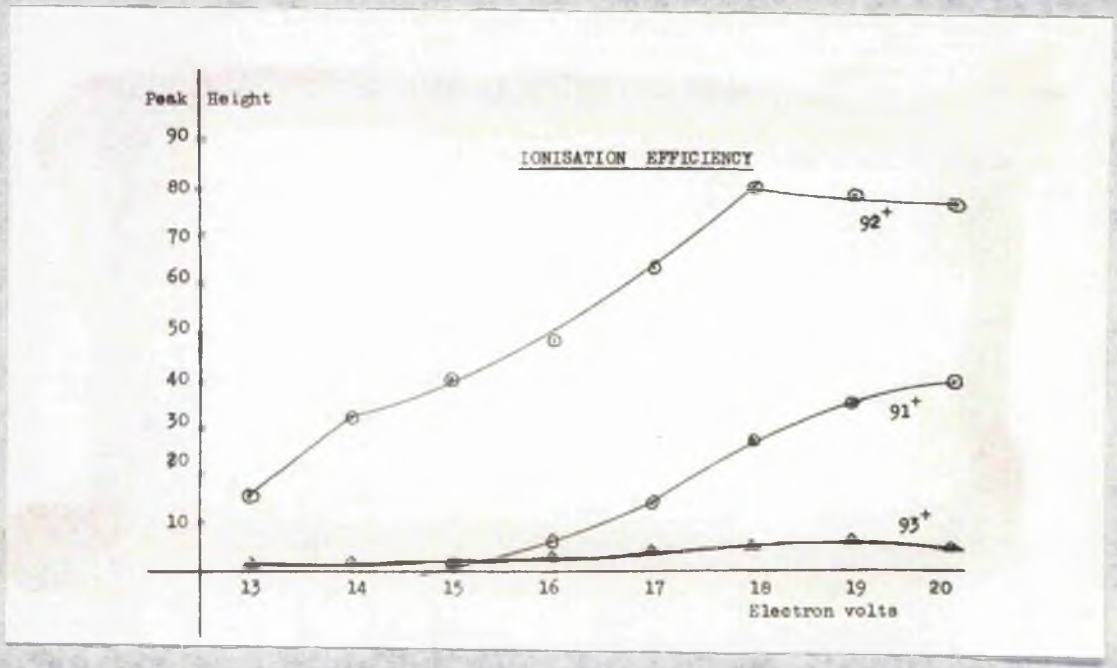
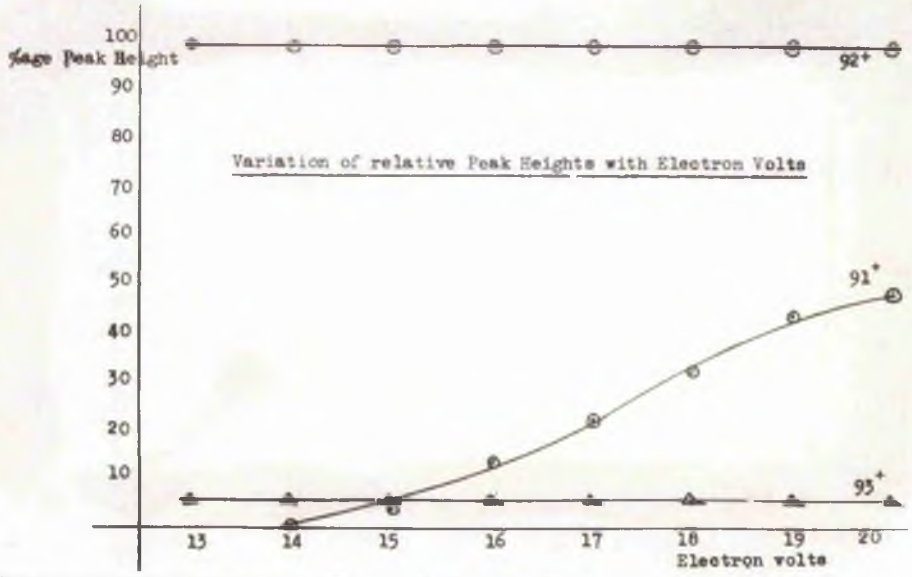

Peak Height
IONISATION EFFICIENCY
90
80
70
60
50
40
30
20
10
92+
91+
93+
13
14
15
16
17
18
19
20
Electron volts

FIGURE XIV


Sage Peak Height
100
90
80
70
60
50
40
30
20
10
Variation of relative Peak Heights with Electron Volts
92+
91+
93+
13
14
15
16
17
18
19
20
Electron volts

Section 2.6

Infra-red spectrometry

It was hoped that the position of the hydrogen atoms exchanged could be found by examination of the infra-red spectrum of the product toluene. The Department had available a Grubb-Parsen GS2A double beam instrument suitable for this purpose.

Many spectra of toluene and deutero-toluenes are reported in the literature. The spectrum of toluene αd_3 has been examined in considerable detail by Wilmshurst and Bernstein.[60] Spectra of deutero-toluenes containing deuterium in the ring have been reported by Turkevich et al[61], Tiers,[62] Tiers and Tiers,[63] Gold and Satchell[64] and Kunst[65] mostly as tools for analysing products of exchange reactions. These results are summarised in the chart (Table II).

There appears to be some disagreement between the authors about the exact positions of the peaks and about which peaks belong to d_0 toluene impurities but a general guide can be obtained. The limitation of some of these spectra is that they refer to deutero-toluenes containing one deuterium atom in the ring and hydrogen atoms in the side chain. In the experiments reported here the products contained many deuterium atoms and the side chain was always fully exchanged before reaction in the ring occurred. The data in Table II can be used to establish whether exchange occurs in the side chain when the very strong peaks at 13.7 and 14.4μ (C-H out of plane deformation) are progressively replaced by a single strong peak at about 14.1μ. It was also used to find if the last two hydrogen atoms exchanged in the ring were ortho to the side chain. In this case the reaction was reversed to give an ortho-deutero-toluene as a final product. This is described below under section 3.4 (Results on nickel films).

Relative intensities of peaks are reported by Tiers and by Kunst and shown on Table II in brackets beside the relevant peaks. The peaks around 4.4μ, the C-D stretching region, are much weaker than the

equivalent C-H stretching peaks at 3.3μ, and very much weaker than the C-D out of plane deformation peaks between 13.5 and 17.5μ.

Difficulties arose in handling the small amounts of toluene concerned. This was usually 1.62 mms. Hg pressure in a 490 ml. reaction vessel at $0^{o}C$ i.e. 4.7×10^{-5} moles. The reaction products were frozen out in liquid air traps and after removal of hydrogen, were transferred to liquid air cooled tubes on B 10 cones. CS_2 was added to the solid in the tube immediately after it was removed from the liquid air and the infra-red spectrum of the resulting solution recorded.

Spectra were taken in a 0.2 mm. path length KBr cell using the normal slit programme from 5-22μ.

The choice of solvent lay between CS_2 and CCl_4. The former obscured the C-D stretching region around 4.4μ but did not affect the 13.5 - 17.5μ region and seemed preferable to CCl_4 which, although it is clear up to 5μ, has an extensive area of total absorption between 11.5 and 14.5μ. Some of the products of the earlier experiments were examined in CCl_4 solution. The difficulties of the relatively low intensities of the 4.4μ peaks coupled with the obliterated region from 11.5 to 14.5μ where more intense peaks occurred, led to the adoption of CS_2 as the solvent.

Section 2, 6

TABLE II

Infra-red Spectra of Deuterium Containing Toluenes

(Relative intensities in brackets)

Source	Compound	11.04	11.5	12.0	12.5	13.0	13.5	14.0	14.5	15.0
Turkevich et al	o-deutero					12.74 13.07	13.79	13.97 14.39		
	m-deutero	10.91 11.19 11.38			12.5		13.79	14.39		
	p-deutero			11.96			13.77	14.08 14.43		
	-deutero							13.99 14.41		
Wilmshurst & Bernstein	toluene						13.70	14.39		
	toluene αD_3			11.83		13.19		14.10 14.39		
Tiers & Tiers	toluene						13.72(280)		14.41 (120)	
	o-deutero				12.9(130)		13.87(109)			
	m-deutero				12.41(103)				14.45(105)	
	p-deutero			11.93(160)				14.08(30)		
Künst	toluene						13.74(510)			
	o-deutero					12.96(192)				
	m-deutero				12.55(142)					
	p-deutero			11.98(192)						
Gold & Satchell	o-deutero				12.9					
	m-deutero				12.55					
	p-deutero			11.95						

EXPERIMENTAL DATA

Section 3. 1

Preliminary Work (Runs 53-69)

Early experiments were carried out with a view to finding the extent of deuteration at temperatures at which exchange occurred. Anderson [66] had reported hydrogenation of toluene on nickel films at temperatures of 45°C. This was confirmed in the present work (see below; Runs 79,80 etc.) while exchange was also found to occur at 0°C. and below. It was therefore thought that the exchange and deuteration processes might be independent as had been reported for benzene.[26,27]

The products of these early reactions were analysed by infra-red spectrometry and by mass spectrometry using high electron accelerating volts. The products were pumped from the reaction vessel to a bulb which was later connected to the mass spectrometer. These results showed in peaks up to m/e = 98, the highest peak being for m/e = 96 for the experiments on nickel; and peaks up to m/e = 98 in smaller amounts with the highest peaks at m/e = 94 and 95 for palladium. The nickel experiments showed deuterated products at masses 104 to 112 while the palladium experiments gave no evidence of deuteration. The infra red spectra of products exchanged on nickel showed new peaks at 4.38, 4.41, 4.54, and 4.69μ, which is the C-D stretching region, indicating ring and side chain-exchange, together with a pattern of peaks from 14μ onwards. These spectra were taken in CCl_4 solution so that the region 12-14μ was obscured. Peaks appeared at 14.05μ, 14.41μ, a group at 15.45, 15.61, 15.76 and 15.95μ and two large peaks at 16.5 and 17μ with occasionally, a peak at 17.6μ. Comparison of these peaks with the table at the end of section 2,6 (Infra-red spectra) together with the mass-spectra, again indicated that exchange had occurred in the ring and side chain on nickel.

In the case of the palladium catalysed exchange the peak at 14.05μ was the strongest peak in the spectrum, indicating side exchange only.* These spectra were taken in CS_2 solution. Experiments to ascertain that the peaks in the spectra were due entirely to the catalyst and pure reactants were performed. The infra-red and mass spectra of the reactants were studied and a blank experiment without a catalyst film was performed. None of the reported peaks were found in these cases.

In view of these results, which were interpreted as exchange throughout the molecule on nickel, and in the side chain only in palladium, the final form of the reaction vessel was evolved and connected to the mass spectrometer directly. The mass spectrometer was then adjusted to function at low electron accelerating volts and a high enough resolution to differentiate the amounts of the exchanged species. It was thus possible to obtain rates from the variation of the percentage of deuterium containing toluenes with time.

Section 3. 2

Method of analysis

The results of run 70 were analysed by the method used by Kemball.[7] This method uses equations similar to equations developed by Harris.[68] The rate is followed by the use of a parameter ϕ, defined as (in the case of toluene) $\phi = d_1 + 2d_2 + 3d_3 + 4d_4 + 5d_5 + 6d_6 + 7d_7 + 8d_8$ where d_1 is the percentage of total toluenes present as $C_7H_7D_1$, d_2 the percentage of $C_7H_6D_2$ etc.. The mean deuterium content is thus $\phi/800$ where the total exchange is considered or $\phi/300$ where the side chain is the only site of exchange, and only the first three terms are relevant.

If all the hydrogens in the molecule were equally susceptible to exchange, and ignoring the influence of isotopes on the rate, the

* p-deutero isomers can be excluded as peaks were not observed at 11.93 and 16.47μ.

course of the reaction would be given by the first order equation

$$d\phi/dt = k_\phi (1 - \phi/\phi_\infty) \qquad \text{EQUA. A.}$$

where k_ϕ is the rate constant equivalent to the number of deuterium atoms entering 100 molecules of the hydrocarbon in unit time after the start of the reaction, and ϕ_∞ is the equilibrium value of ϕ. Integration of this equation gives

$$-\log_{10}(\phi_\infty - \phi_t) = k_\phi t/2.303\phi_\infty - \log_{10}(\phi_\infty - \phi_o) \qquad \text{EQUA. B}$$

where initially $\phi = \phi_o = 0$, Kemball[7] states that these equations are obeyed in a great variety of exchange reactions. Failure of the equations may be due to different reactivities of the hydrogens in the molecule or to poisoning of the catalyst.

A second rate constant k_o can be found representing the initial rate of disappearance of the light hydrocarbon C_7H_8 in percentage per unit time. This is obtained from the empirical first order equation:-

$$-\log(x_o - x_\infty) = k_o t/2.303(100 - x_\infty) - \log(100 - x_\infty)$$

$x_\infty > 0$ for the experimental conditions found in the present work

$$\therefore \quad -\log x_o = k_o t/230.3 - \log_{10} 100 \qquad \text{EQUA. C}$$

where x_o is the percentage of C_7H_8 present at time t. and where the final amount of C_7H_8 is zero, as found in these experiments.

The ratio of these two constants $M = k_\phi/k_o$ represents the mean number of hydrogen atoms replaced by deuterium atoms in each molecule of C_7H_8 undergoing exchange in the initial stages of the reaction. Kemball then warns that these rate constants are constant for a single mixture of reacting gases and are dependent on pressure, differing if

the pressure of the reactants is altered.

In a later paper Kemball and Crawford[31] considered the exchange of alkyl benzenes which show differing hydrogen reactivities. These reactivities could be found from equation B by plotting log $(\phi_\infty - \phi)$ versus t. when two approximately linear sections of the graph were found, in the case of p-xylene, corresponding to the side chain (A) and ring (B) hydrogens.

The gradient of the first section gave k_ϕ and is the sum of the initial rates of exchange of the two hydrogen atoms i.e. $k_\phi = k_A + k_B$ while the final part can be represented by the equation

$$- \log (\phi_\infty - \phi) = k_B t/2.303\phi_{B\infty} - \log \phi_{B\infty} \qquad \text{EQUA. D.}$$

assuming group A hydrogen atoms to have attained their equilibrium state.

$\phi_{B\infty}$ is defined by the relations

$$\phi_\infty = \phi_{A\infty} + \phi_{B\infty} \text{ and } \phi_{A\infty} / \phi_{B\infty} = n_A/n_B$$

where n_A and n_B represent the number of hydrogen atoms in the two groups i.e. 6 and 4 for p-xylene. Kemball defines three groups of hydrogen atoms:

Group A: hydrogen atoms on carbon atoms α to the benzene ring and atoms on the ring not ortho to a side group.

Group B: hydrogen atoms on the ring ortho to one but not two side groups.

Group C: hydrogen atoms on carbon atoms β and γ to the benzene ring (and in m-Xylene the atom on the ring between the methyl groups), so that in the case of toluene two reactivities could be expected, which Kemball found. He also found the group A atoms on toluene to split into two groups of three which he inferred as being side chain and ring.

Another equation modified from equation B was also derived by Kemball.

$$-\log (C_n - \phi) = k_A t/2.303 C_n - \log_{10} C_n \qquad \text{EQUA. E}$$

where C_n represents the value of ϕ_∞ expected for the exchange of the n group A atoms. This implies groups B and C can be neglected. In the case of p-xylene quoted in this paper the plots using n = 6 and n = 7 were curved away from each other indicating a non-integral value of n. This indicates the contribution of the group B atoms to the value of ϕ_∞ .

Kemball then summarises the principal methods of identifying the groups of hydrogen atoms in each hydrocarbon as:

1. Inspection of the distribution of isotope species during exchange.

2. The use of equations B and D or corresponding (modified) equations where 3 groups of hydrogen atoms were found.

3. The use of equation E to determine the number of hydrogen atoms in the most easily exchange group.

This kind of analysis, modified to suit the reaction conditions, was used in the present research to determine reaction rates and relative reactivities, but was complicated in that toluene contains two groups of 3 type A atoms (side chain and ring) and two group B atoms (ortho to the side chain). Infra-red evidence, not used by Kemball, made the identification of the site of exchange easier in the present work.

Determination of ϕ and ϕ_∞

ϕ was found from the mass spectrometer peak heights in the way described above (section 2.5). Each quantity of d_1, d_2 etc. toluene was found to the nearest 1/2%. Values of ϕ_∞ depended on whether the reaction could be seen to go to completion. On palladium (Runs 70 II, IV),

a consistent value of ϕ_∞ could be found with the expected error from the final equilibrium figures. Kemball remarks on the difficulty of obtaining ϕ_∞ as this is not the theoretically expected value.

In the investigations reported here the values of ϕ_∞ are the values found by experiment. ϕ_∞ in the case of the side chain exchange only, was found on palladium over a series of experiments at 293°K and ϕ_∞ in the case of total exchange, was found on nickel in special experiments on heavy films (Runs 90 and 91). In the latter case the experiment had to reach equilibrium well within the time limit of two hours necessary to avoid alteration of the mixture by the leaking of gas to the mass spectrometer, and hydrogenation had to remain insignificant. These two experiments provided a reasonable figure for ϕ_∞ of 687 (run 90) and 683 (run 91) for a 10:1 D_2: toluene mixture. As experiments on iron did not reach equilibrium in a reasonable time this value was also used for the results on iron.

Experimental errors

In each case the amount of each exchanged toluene and of the original toluene was calculated as a percentage of total toluenes to the nearest 1/2%. Addition of all these percentages never varied from 100% by more than 1% so that each value could be given an average error of $\pm$ 1 (the total number of toluenes present %) e.g. in the case of the exchange on palladium

$$\phi = d_0 + d_1 + d_2 + d_3 = 100 \pm 1\%$$

so the average error in d_0, d_1 etc. = 1/4%

Thus in calculating $\phi = d_1 + 2d_2 + 3d_3$ the error in $\phi = \pm$ 1 1/2 in 300.

The value found for ϕ_∞ was 279 for the ratio pD_2/pC_7H_8 = 10/1 on palladium. Since log $(\phi_\infty - \phi_t)$ was plotted versus time values of $(\phi_\infty - \phi_t)$ less than 3 would be unreliable. On nickel values of d_1, d_2 etc. also added up to 100 ± 1%. As d_8 only appeared after d_0 had vanished the average error was then 1/8% and $\phi = d_1 + 2d_2 + 3d_3 + 4d_4 + 5d_5 + 6d_6 + 7d_7 + 8d_8$ gave errors in ϕ_∞ of ± 4 1/2 in 800 and values of $(\phi_\infty - \phi)$ less than 9 would be unreliable. This applied to the values of ϕ_∞ which were found to be 740 and 685. The value of ϕ_∞ = 471 which was found when using a pressure ratio of D_2:toluene of 10:2 never involved the d_8 molecule so that $\phi_\infty = 471^{+}- 3$ 1/2 and values of $(\phi_\infty - \phi_t)$ less than 7 were unreliable.

Values of k were found by drawing the best straight line through the points calculated from the data and plotted on the $\log(\phi_\infty - \phi_t)$ versus time graph. Determination of best lines by the least squares method in two cases showed the lines drawn by eye to be very close to the lines obtained from the least squares calculation. In addition as the graphs are considered to have two linear sections joined by a bend, use of the least squares method involves deciding which points belong to the linear sections and which to the bend. Because of this the least squares method was discarded.

It was clear from examination of the graphs of log $(\phi_\infty - \phi_t)$ versus time that the concordance of the points gave values of k_ϕ which could not have been in error by more than a few percent for large values of $(\phi_\infty - \phi_t)$, but as $(\phi_\infty - \phi_t)$ became smaller the error rose considerably. Less importance can therefore be placed on values of k_ϕ obtained for the replacement of the final two hydrogen atoms in the ring.

In all cases variation of k_ϕ from one preparation of catalyst to another exceeded the apparent systematic error by a large amount.

TABLE III

Results on Palladium Films

Run No.		Wt. of film	Temp. of Reaction	Energy of Activation (Kcal)	ϕ_α	k_ϕ(side chain)	k_0(all x 10^{-2}
70	I	33 mgm.	273°k		279	0.66 x 10^{-2}	0.56
71	I	22.8 mgm.	"		"	2.2 x 10^{-2}	1.4
71	II	"	"		"	"	1.4
72	I	23.5 mgm.	"		"	0.81 x 10^{-2}	0.62
	II	"	"	4 kcal. (I+III)	"	0.73 x 10^{-2}	0.62
	III	"	293	5 kcal. (II+IV)	"	1.4 x 10^{-2}	1.2
	IV	"	"		"	1.4 x 10^{-2}	1.1
76	I	36 mgm.	273		"	1.1 x 10^{-2}	0.68
				10	685	0.75 x 10^{-2}	
	II	"	293		"	2.6 x 10^{-2}	-
77	I	10.7 mgm.	273		279	1.5 x 10^{-2}	1.1
	II	"	293	18	"	1.5 x 10^{-2}	6.6
	III	"	273		"	1.4 x 10^{-2}	0.89
	IV	"	293	16	"	10 x 10^{-2}	4.3
	V	"	273		"	1.6 x 10^{-2}	1.05
	VI	"	293	14	"	8.8 x 10^{-2}	5.2
	VII	"	273	9 (VII+VIII)	"	1.4 x 10^{-2}	1.0
	VIII	"	293		"	4.1 x 10^{-2}	2.55
	IX	"	293	12 (VII+IX)	"	6.7 x 10^{-2}	4.2
78	I	33.6 mgm.	293		685	2.5 x 10^{-2}	-
	II	"	319		"	-	-
	III	"	332		"	-	-
	IV	"	342		"	-	-

D_2/toluene pressure ratio was constant at 10:1 for all reactions k units atoms (100 molecules)$^{-1}$ (

This must be put down to irreproducibility of preparation of the catalyst films.

Section 3, 3

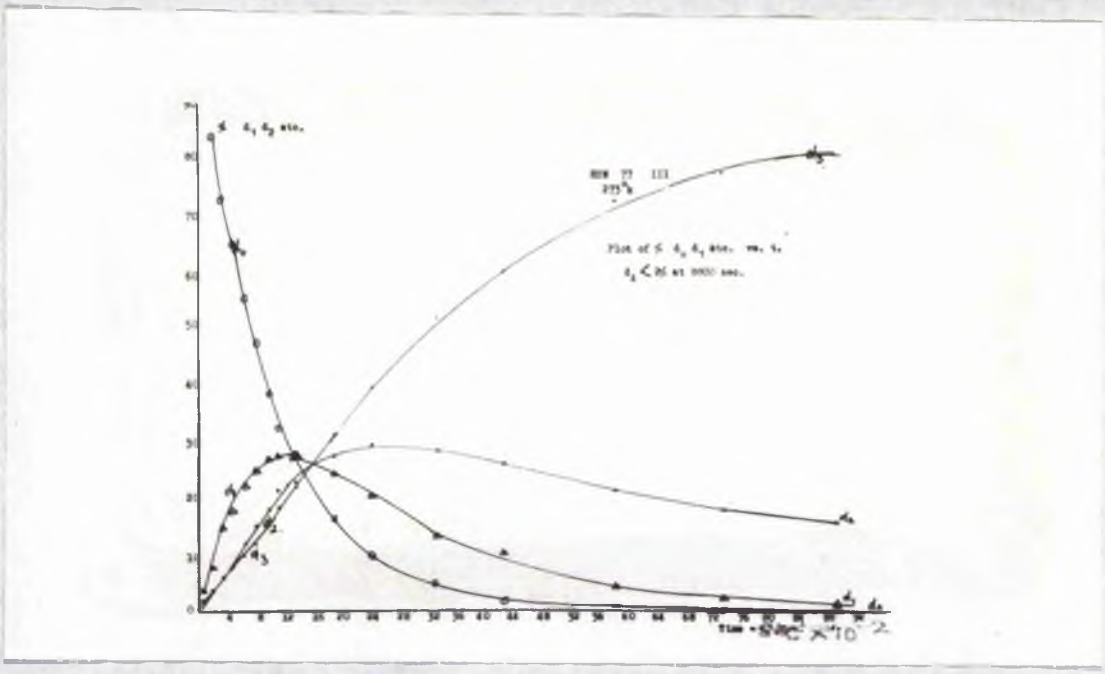
Results on Palladium films

Experiments were performed on palladium films varying in weight from 10.7 to 36 mgm. and at temperatures from 275°K to 342°K. The amounts of the gases are the same as those given for nickel (below) for a 10 D_2 to 1 C_7H_8 mixture.

These results are summarised in Table No. III.

The reaction at 275° led to exchange in the side chain with only a small amount of exchange in the ring except in the heavy films (Runs 76 and 78). The value of ϕ_∞ for the side chain reaction was taken as the average value 279 that is 95% exchange for a 10 D_2 to 1 C_7H_8 mixture. Typical graphs of d_1, d_2 against time at 275°K and 293°K are shown in Figures XV & XVI (Runs 77, III and IV). As can be seen equilibrium is just attained in the low temperature case and very clearly attained in the high temperature case. No correction was made to ϕ_∞ for variation with temperature. Ring exchange in these cases was limited to less than 2% of total toluenes at the end of the reaction. Values of M are all slightly greater than unity. In some cases a large number of experiments were conducted on one film to find the relative reproducibility of catalyst and reactant preparations. A run number was used to indicate a film preparation, a Roman numeral indicates the serial number of the experiment performed on that film. The 10.7 mgm. film prepared for Run 77 was used nine times and showed a general, but not regular fall off in activity with use, but there is less overall reproducibility from one film to another than that shown between successive experiments on the same film.

FIGURE XV


Plot of S d_1 d_2 etc. vs. t.
d_1 < 25 at 9900 sec.
Time - Sec X 10^-2

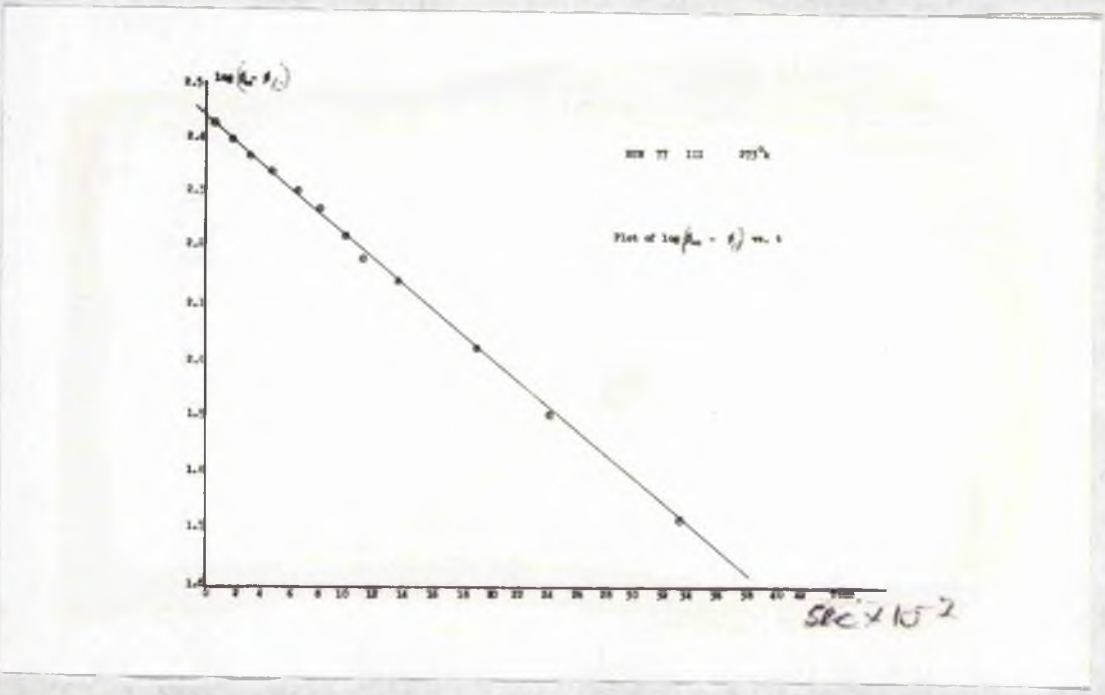
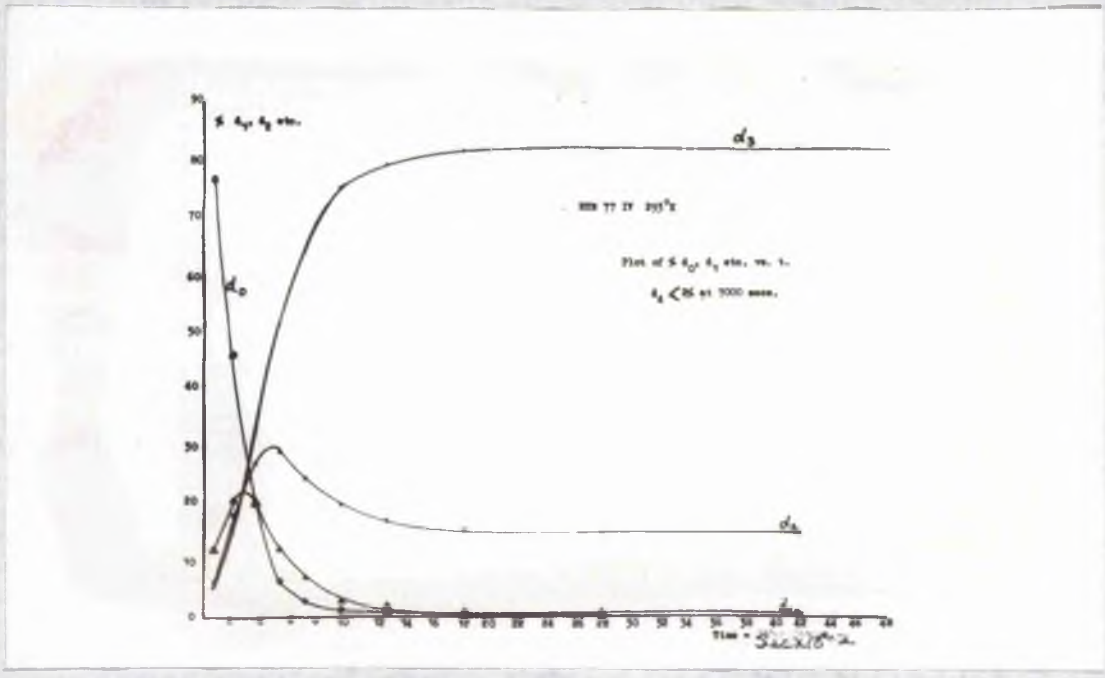
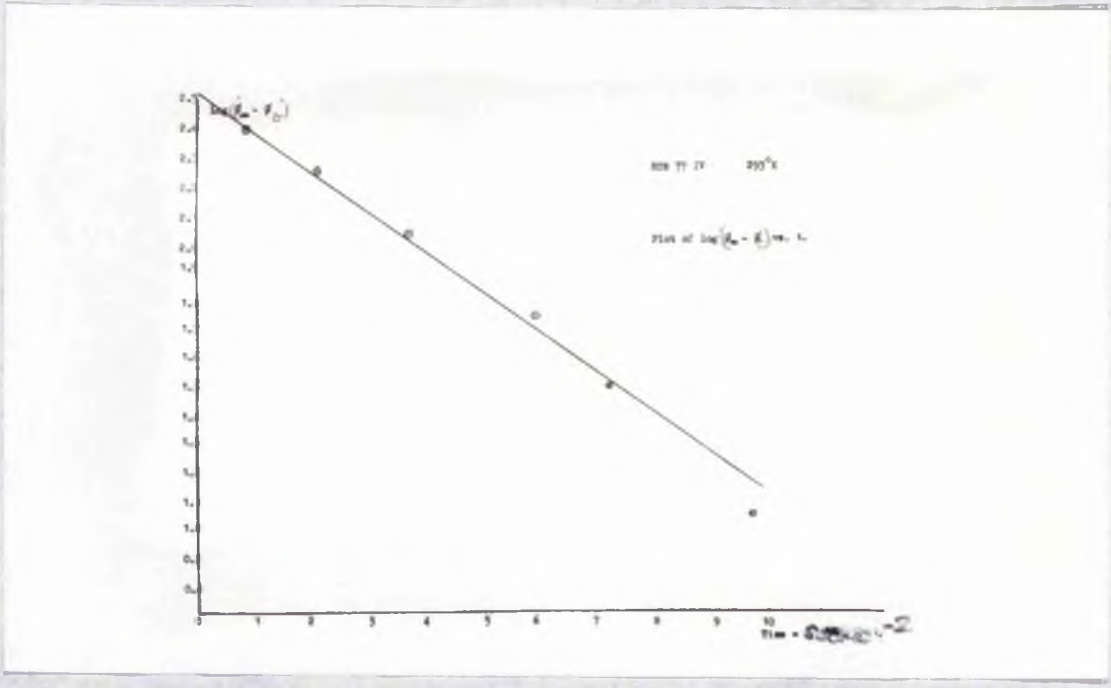

Plot of log(d∞ - d1) vs. t
Sec X 10^-2

FIGURE XVI


Plot of δ_0, δ_1 etc. vs. t.
δ_3
δ_0
δ_2
δ_1
Time - Seconds


Plot of $\log(\delta_\infty - \delta)$ vs. t.
Time - Seconds

It is also seen that reactivity decreased more rapidly at 293° than at 273°K.

Run 77		I	III	V	VII
273°K	k_ϕ	1.5×10^{-2}	1.4×10^{-2}	1.6×10^{-2}	1.4×10^{-2}

Run 77		II	IV	VI	VIII
293°K	k_ϕ	1.5×10^{-1}	1.0×10^{-1}	$.88 \times 10^{-1}$	$.41 \times 10^{-1}$

IX
$.67 \times 10^{-1}$

and that values of M are fairly constant at 273°K and fall at 293°K.

273°K	1.35	1.6	1.5	1.4	
293°K	2.25	2.3	1.7	1.6	1.6

In Runs 76 and 78 exchange occurred in the ring following the side chain exchange. It was shown in the case of nickel (above) that ϕ_∞ was 685 for this reaction (ratio of D_2 to C_7H_8 = 10:1). The system could not be brought to equilibrium in a reasonable time even at high catalyst temperature (Run 78) and therefore the value for ϕ_∞ obtained when using the nickel catalyst, was used. If the reaction had been allowed to proceed to equilibrium the time taken would have been such that the fractionation of deuterium and toluene leaking through into the mass spectrometer would have led to a significant loss in total gas pressure as well as an unreasonable difference in the ratio of deuterium to toluene from that originally put on to the catalyst.

It is interesting to compare values of k_ϕ obtained from the early values of log $(\phi_\infty - \phi_t)$ vs. t using the palladium value of ϕ_∞ for the side chain reaction only (279) and the nickel value for the complete exchange (685). In Run 76 where this was possible values of k_ϕ for the side chain exchange were found to be

$\phi_\infty = 685$ $\quad k_{\phi_{SC}} = 7.5 \times 10^{-3}$ atoms/100 molecules/sec/mgm Pd.

$\phi_\infty = 279$ $\quad k_{\phi_{SC}} = 1.1 \times 10^{-2}$ " " "

It should be noted that in each case the reactivity found for the ring hydrogen atoms was considerably less than the side chain hydrogen atoms (as found by Kemball [31] on nickel).

Infra-red analysis of the products showed the exchange of the first three hydrogen atoms to be the side chain atoms by the appearance of the peak at 14.1μ. The site of exchange in the ring could not be identified definitely, (Runs 76 and 78) other than by comparison with later nickel results. By using data from reactions at 273° and 293°, as in Runs 72, 76 and 77, values of activation energy have been found. With such a small temperature range the inaccuracy in the determination of the energy of activation is naturally considerable. These results are shown in the table.

Deuteration did not appear to occur at the lower temperatures. After 3 hours at 342°K (Run 78 IV) hydrogenation was negligible as judged by the peaks at masses 104 to 112 (0.1% of the total hydrocarbons). In view of Harper and Kemball's[36] results it is interesting to notice that the deuterium content of the methylcyclohexanes at the end of the reaction does not correspond to an addition of 6 deuterium atoms, but appears to correspond to an

TABLE IV

Results on Nickel Films

Results for a Deuterium to Toluene ratio of 10:1

Run No.		Wt. of film	Reaction temp.	ϕ_∞	k_0	k_ϕ side chain	k_ϕ ring 3	k_ϕ
79	I	26.2	273	685	-	-	2.1×10^{-2}	3.3
	II	"	293	"	-	-	-	1.5
80	I	23.5	273	"	-	-	3.1×10^{-2}	5.1
	II	"	293	"	-	-	-	1.5
81	I	15.6	273	"	-	-	6.6×10^{-2}	3.7
83	I	12.1	317	"	-	-	1.1×10^{-1}	9.3
	II	"	273	279	4.1×10^{-3}	7×10^{-3}	-	
90		35.4	293	685	-	-	-	2.8
91		45.0	293	"	-	-	-	2.1
(92)		(3.3)	(293)	(")	(5×10^{-2})	(4.7×10^{-2})	(1.8×10^{-2})	
101		5.0	293	"	1.6×10^{-2}	1.5×10^{-2}	5×10^{-3}	
102		9.7	293	"	-	-	1.3×10^{-1}	1.5
103		9.3	273	"	3×10^{-2}	2.5×10^{-2}	2.1×10^{-2}	4.4
110		16.2	273	"	-	-	-	5.7

k units atoms $(100 \text{ molecules})^{-1} (\text{mgm Ni})^{-1} \text{ sec}^{-1}$

addition of about 6.5 deuterium atoms to the toluenes examined at the same time. It would therefore appear that some exchange has occurred during or after the deuteration reaction. The deuterium: hydrogen ratio was calculated in each case and found to be in agreement with the total percentage exchange within experimental error.

Section 3. 4

Results on nickel films

Experiments were carried out on nickel films varying in weight from 3.3 to 45 mgm., mainly at 273°K or 293°K and with differing ratios of partial pressures of deuterium and toluene. These results are summarised in Table No. IV.

The course of the reaction was very different from the reaction on palladium films. Only in a few cases could the reaction rates be ascribed solely to the side chain. Typical plots of the different exchanged species and log $(\phi_\infty - \phi_t)$ with time are shown in Figures XVII to XX. The proportions of exchanged species varied with the toluene: deuterium ratios so that ϕ_∞ was determined empirically for each mixture. In the 10 : 1 ratio case this was found in Runs 90 and 91 as outlined above. In the 20:1 ratio case equilibrium was seen to be reached in Run 99 at a value of 740 $\pm$ 4 1/2 which agreed with remaining experiments. The 10:2 deuterium to toluene ratio gave an equilibrium value of = 471 $\pm$ 3 1/2. The final hydrogen: deuterium ratios confirmed these figures where the reaction reached equilibrium. k_ϕ determined from the slopes is the addition of the various k_{ϕ_A} values as Kemball explains (above Section 3.2).

k_ϕ^{I} = k_ϕ sidechain and k_ϕ ring(3) and k_ϕ ring(2)

k_ϕ^{II} = k_ϕ ring(3) and k_ϕ ring(2)

k_ϕ^{III} = k_ϕ ring(2)

TABLE IV contd.

Results for Deuterium to Toluene ratio of 20:1

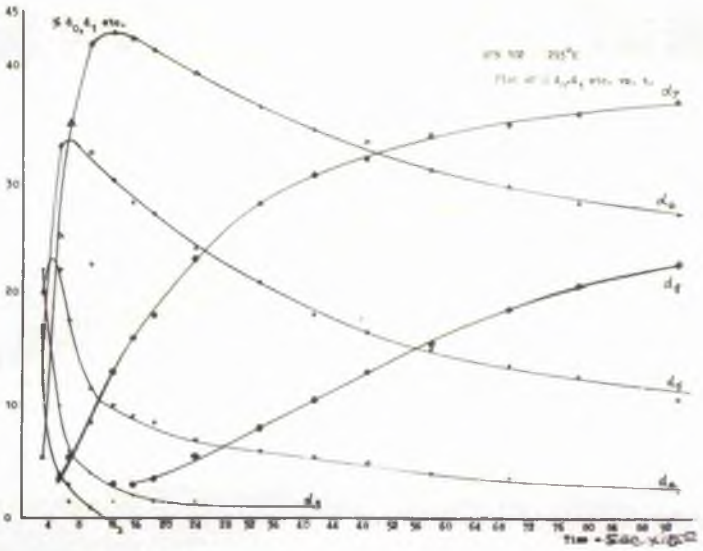
Run No.	Wt. of film	Reaction temp.	ϕ_∞	k_0	k_ϕ side chain	k_ϕ ring 3	k_ϕ
94	13.9	273	740	-	-	4.5×10^{-2}	7.2
95	17.1	273	"	-	-	7.6×10^{-2}	6.8
98	31.2	293	"	-	-	-	2.9
99	29.3	293	"	-	-	-	3.3
100	7.8	293	"	-	-	1.6×10^{-1}	1.2

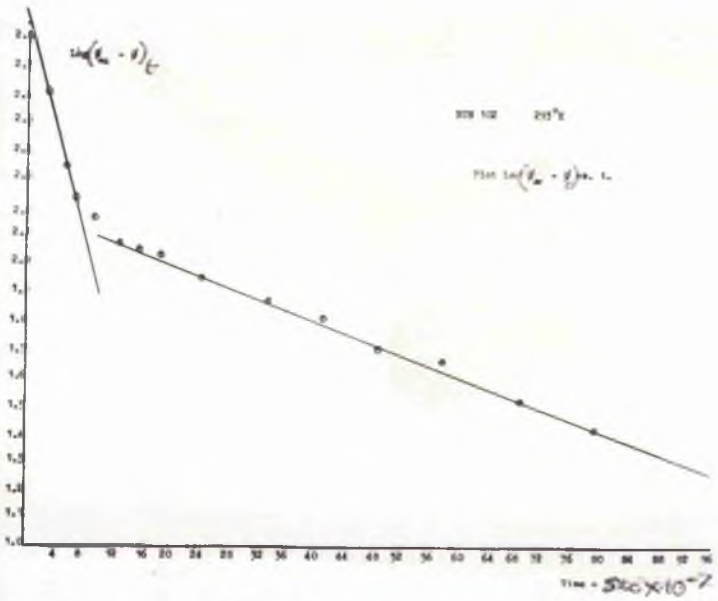
Results for Deuterium to Toluene ratio of 10:2

109	10.9	273	471	2×10^{-3}	2.2×10^{-3}	-	
111	28.8	273	"	8×10^{-3}	1.5×10^{-2}	-	
112	8.8	293	"	4×10^{-2}	4.8×10^{-2}	1.2×10^{-2}	
113	9.1	293	"	5×10^{-2}	6.9×10^{-2}	1.1×10^{-2}	

k units atoms 100 molecules^{-1} mm Hi^{-1} sec^{-1}

FIGURE XVII





Values of k_g quoted in the table for particular parts of the molecule are determined by subtracting the appropriate k_g values for further reaction, (where this had been found).

It was found that successive experiments rapidly poisoned the catalyst in most cases. Runs 79 III, 80 III, 81 II, and 83 III did not show any reaction at all and Run 83 II can be seen to have been very slow compared with Run 83 I. As with palladium it is noted that higher reaction temperatures caused greater poisoning. Results of Runs 79 II, 80 II, and 83 II are thus suspect although the values in Runs 79 II and 80 II are in fair agreement with Runs 90, 91, and 102. Runs 83 I disagrees with Run 102, and Run 101 appears to have been on a poisoned film when it is compared with the others. This may have been due to inadequate degassing of the new nickel filament used to prepare this film. Results on this catalyst and in Run 83 II show the exchange in the side chain very clearly and suggest values of M in the case of poisoned catalysts. Energies of activation had to be found from values at 275° and 293°K as temperatures greater than 293°K tended to cause more hydrogenation, than the final 1% considered the maximum allowable before alteration of the gas mixture would have affected the reaction. The energies so calculated were:

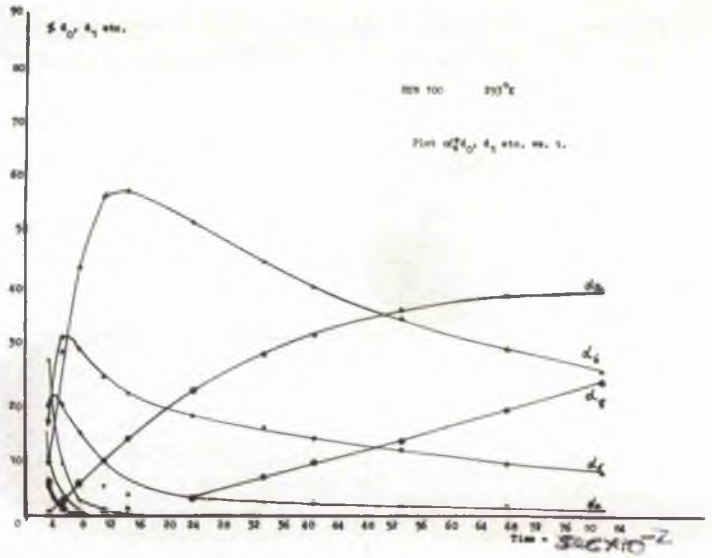
		20:1 ratio	10:1 ratio
Entry into last two atoms of ring	E_{Act}	10 Kcal/mol	12 Kcal/mol
		20:1 ratio	10:1 ratio
Entry into first three atoms of ring	E_{Act}	8 Kcal/mol	10 Kcal/mol
		10:2 ratio	
Entry into side chain H atoms	E_{Act}	8 Kcal/mol	

The reaction vessel used (with the exception of Run 92) had a volume of 489 ml. The number of moles of deuterium and of toluene admitted to the catalyst at 273°K was 4.6×10^{-4} and 4.6×10^{-5} moles respectively at pressures of 16.5 and 1.65 mm. Hg. respectively in the case of the 10:1 ratio. For the 20:1 ratio the deuterium was 9.2×10^{-4} moles and for the 10:2 ratio the toluene was 9.2×10^{-5} moles. A different reaction vessel was used for Run 92 with a volume of 266 ml. giving 3.7×10^{-5} moles toluene and 3.7×10^{-4} moles deuterium in contact with the catalyst at pressures of 2.6 and 26 mms. Hg. respectively.

At the end of each reaction the final hydrogen:deuterium ratio agreed (within experimental error) with the value to be expected from the final value of f_∞ found. Only in a few cases did the reaction mixture reach equilibrium.

In order to establish that the two least reactive hydrogen atoms were those ortho to the side group, infra-red spectra which could be compared with spectra available in the literature (section 2,6 above) had to be obtained. Literature spectra referred to the exchange of one hydrogen atom only. The reaction (Run 94) was therefore allowed to proceed as near to completion as possible. A check on the masses of the toluenes resulting revealed that the mixture contained a reasonable account of d_7 and d_8 molecules. The products were then frozen down on to the film in liquid air, the deuterium pumped off and replaced by pure hydrogen. The reaction vessel was warmed up again and the reaction proceeded to a new equilibrium checked by mass spectrometry. The spectrum of the resulting product contained a strong peak at 13.0μ with weak peaks at 12.55 and 12.0μ. The experiment was repeated (Run 96) but the mixture this time was allowed only to react as far as d_6 molecules and then reversed as above. The resulting spectra showed peaks at 12 and 12.55μ but no peak at 13μ. According to the summary (section 2,6) this would correspond to the residual ortho deutero-toluene with some meta and para isomers in Run 94 and meta and para isomers but no ortho in Run 96.

FIGURE XVIII



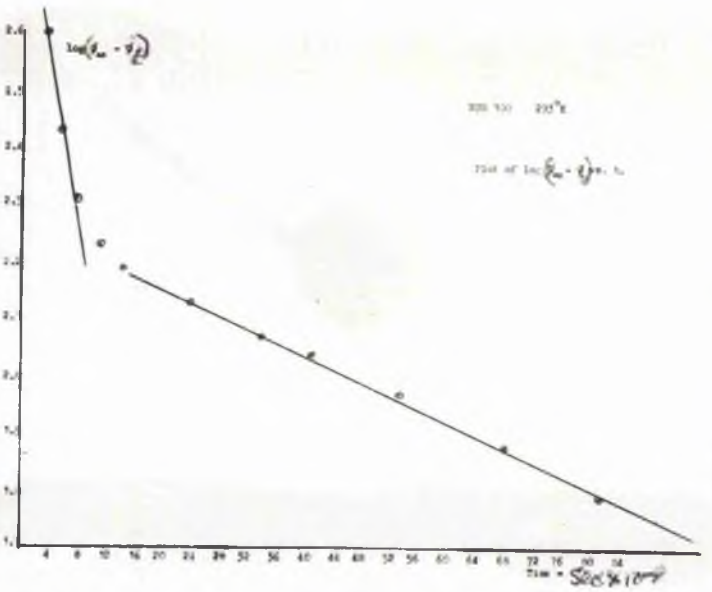
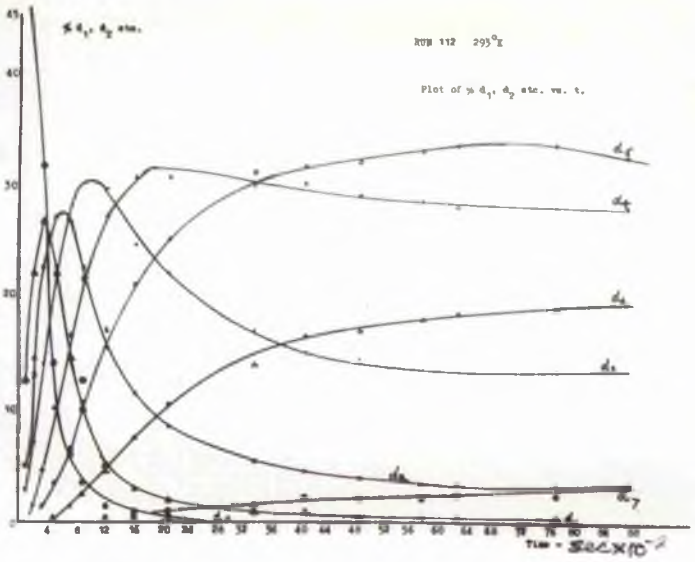
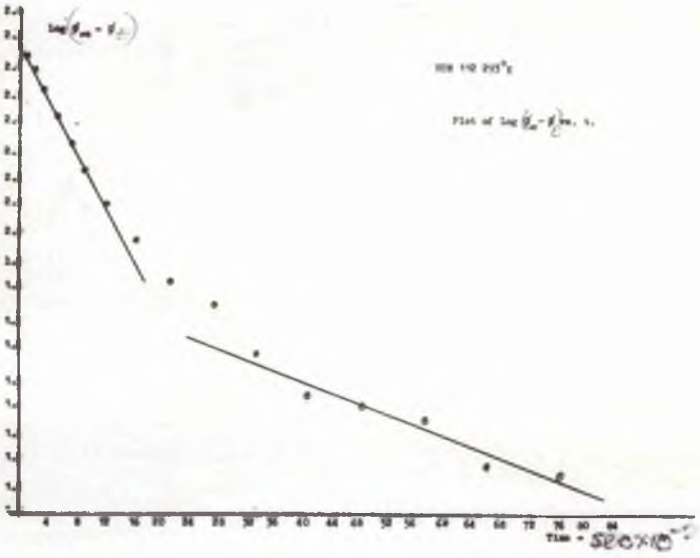


FIGURE XIX


RUN 112 293°K
Plot of % d_1, d_2 etc. vs. t.
Time - Sec x 10⁻²

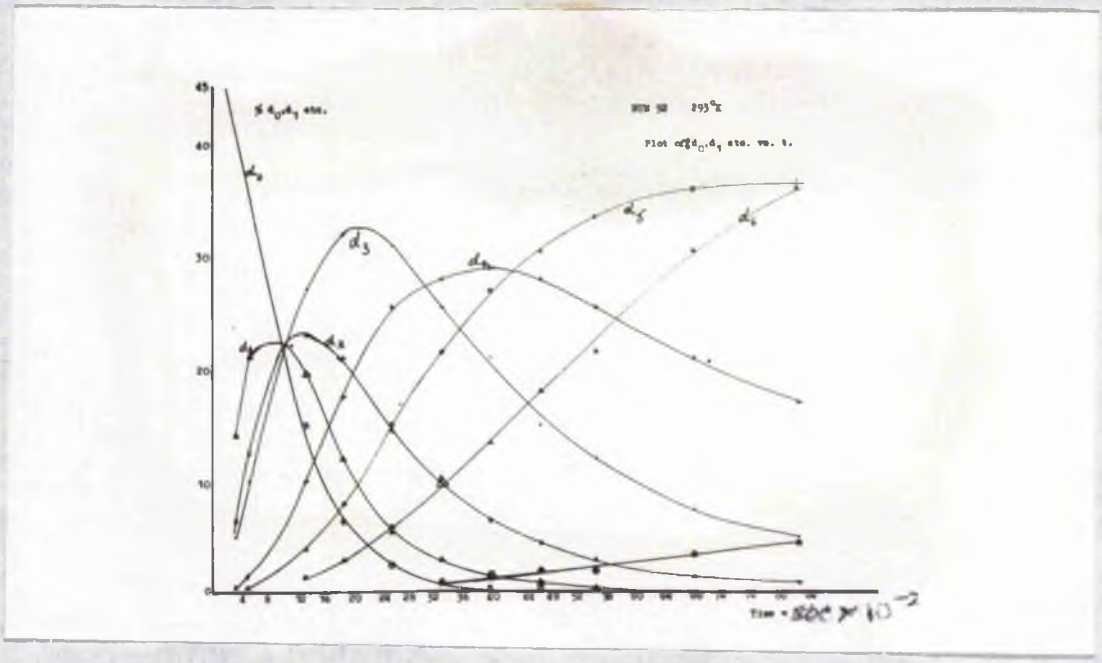

Plot of Log ($\theta_\infty - \theta_t$) vs. t.

This would appear to show that the least reactive hydrogens in toluene are those ortho to the side group. The infra-red spectra of each product mixture could be related to the final mass spectral analysis, certain features of the peaks beyond 14μ changed with increased deuterium content. When a small amount of ring exchange had occurred, peaks at 16.42μ and 16.94μ appeared. As the ring exchange proceeded these gradually gave way to peaks at 18.1 and 18.6μ.

Hydrogenation as judged by the formation of peaks in the mass range 104 to 112(when using 50 volt electrons) occurred in all cases where reaction to form d_7 and d_8 isomers occurred. Reaction was stopped when the amount neared 1% of total hydrocarbons but this was only necessary in a few cases. The rate of production of deuterated methyl cyclohexanes depended on the hydrogen pressure and was troublesome in the 20:1 ratio cases and almost negligible in the 10:2 ratio cases.

Run 92 in reaction vessel 4 can be seen to be slower than other reactions at that temperature and using the same ratio of reactants. Since reaction vessel 4 was smaller than the others it was possible to obtain an increased pressure of reactant applied to the catalyst and it was hoped to deduce the effect of this on the rate. The result is not a clear demonstration of the effect since it should be noted that the catalyst was evaporated on to a much smaller area so that its effectiveness need not have been comparable with other films. Figures XVII to XX show graphs of % d_1, d_2 etc. versus t. for Runs 92, 100, 102 and 112. These show the different courses of the reaction when the reactant pressures were varied. Runs 100, 102 and 112 were conducted on films of similar weight while 92 was a film of about 1/3 their weight and appears as a slower reaction but when corrected for the weight factor is slightly faster. The rate constants are compared in Table V and will be discussed below (section 4). It should be noted that Runs 79 II and 80 II were the second runs on the film and that Runs 90 and 91 were very heavy films.

FIGURE XX


Σ $d_0 d_1$ etc.
Run 58 293°K
Plot of d_0, d_1 etc. vs. t.
d_0
d_1
d_2
d_3
d_4
d_5
d_6
Time - sec × 10^{-2}

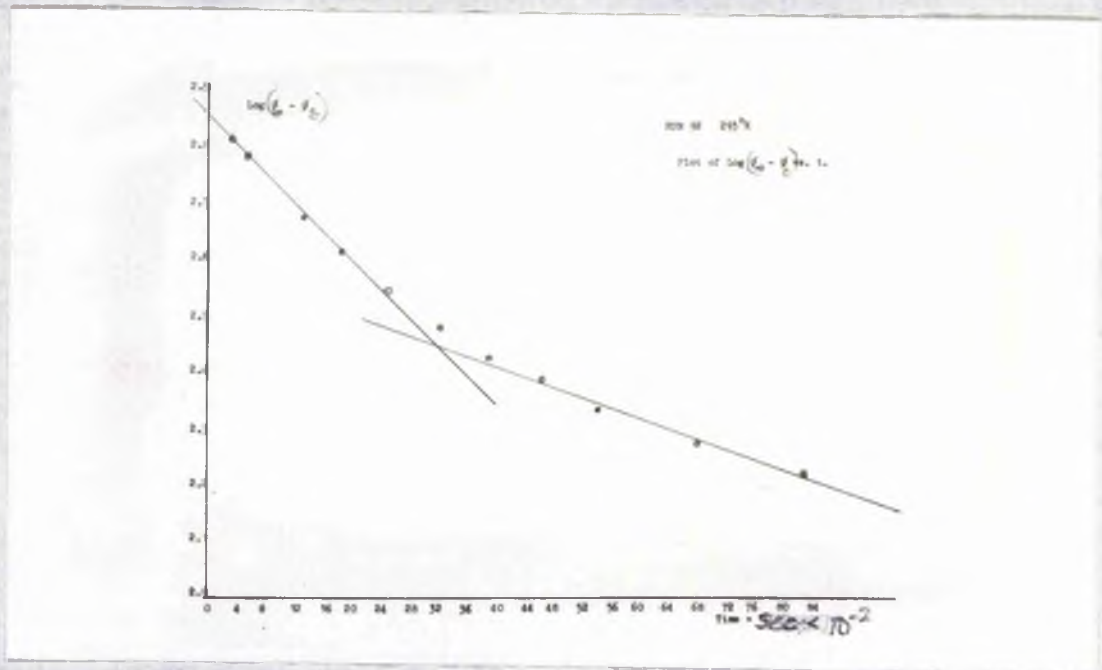

$\log(d_0 - d_\infty)$
Run 58 293°K
Plot of $\log(d_0 - d_\infty)$ vs. t.
Time - sec × 10^{-2}

TABLE V

Comparison of rate constants at 293°k. on Nickel Film

Run	Ratio of reactants	k_{ϕ_2} (ring 3)	k_{ϕ_3} (ring 2)
79 II	10:1		1.5×10^{-2}
80 II			1.5×10^{-2}
90			2.8×10^{-2}
91			2.1×10^{-2}
102		1.3×10^{-1}	1.5×10^{-2}
98	20:1		2.9×10^{-2}
99			3.3×10^{-2}
100		1.6×10^{-1}	1.2×10^{-2}
112	10:2	1.2×10^{-2}	
113		1.1×10^{-2}	

k units atoms (100 molecules)$^{-1}$ (mgm Ni)$^{-1}$ sec^{-1}

TABLE VI

Results on Iron Films

Run No.	Wt. of film	Reaction temp.	ϕ_∞	K_0	k_{ϕ_1} side chain
84 I	21.4 mgm-	273	685	-	4.5×10^{-2}
84 II	"	293	685	1.5×10^{-2}	1.7×10^{-2}
85	2.4	293		No reaction	
86	2.0	293	279	2.15×10^{-3}	3.2×10^{-3}
87	11.8	293	279	4.6×10^{-4}	5×10^{-4}
88	7.4	293	685	-	1.3×10^{-1}
89	10	293	685	-	1.5×10^{-1}
104	16.4	273	685	-	1.2×10^{-1}

Ratio of Toluene : Deuterium 1:10 throughout k units atoms (100

From values of ϕ_∞ it is easy to deduce the percentage deuterium in the 'hydrogen' atoms of the toluene i.e. $(\frac{D}{D+H}) \times 100$ for toluene. Thus $\phi_\infty = 685$ corresponds to 685 replacements by deuterium atoms of the original 800 H atoms in 100 molecules of toluene, and implies 85.5% D in the toluene. This value was produced when (pD_2/p toluene) = 10/1 i.e. an atom ratio of 20/8. If the deuterium had been distributed equally between the final toluene and hydrogen molecules then each chemical compound would have had $\frac{20}{28} \times 100 = 71.5\%$ deuterium. Thus the equilibrium position appears to favour enrichment in the toluene. The full data on this point are shown below :

pD_2/p tol) used	$\frac{10}{2}$	$\frac{10}{1}$	$\frac{20}{1}$
(α) %D for equal distribution	55.5	71.5	83.3
(β) %D found in toluene	59	85.5	92.5

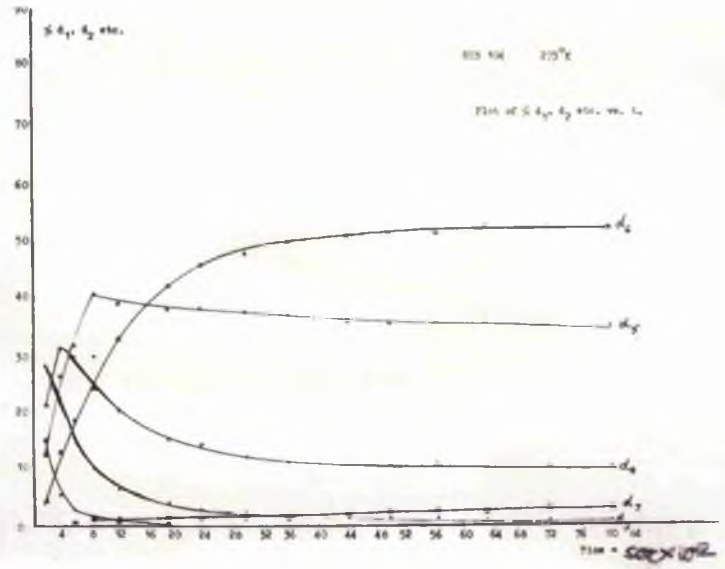
With an original pD_2/p tol. of $\frac{10}{2}$ it is clear we could not envisage a higher degree of exchange than d_4 to d_5 on the average. This can be seen in data for Run 112 (Figure XIX) while in Run 102 (Figure XVII) with a $\frac{10}{1}$ initial ratio the higher degree of exchange is quite evident. The effect of increasing the deuterium pressure is less well marked (Run 100 Figure XVIII).

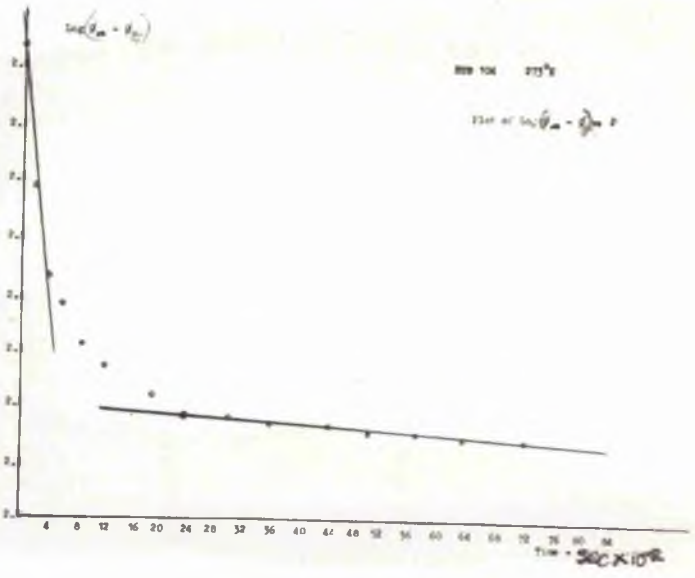
Section 3. 5

Results on Iron films

Some results were obtained on iron films of 2.0 to 21.4 mgm. weight. Difficulty in preparing films was encountered as outlined above (section 2.4). These results are summarised in Table VI. Runs 84 II, 85, 86, and 87 show some poisoning from an unknown source. As Runs 85 and 86 were from previously used filaments it is unlikely that this was due to inadequate degassing of the filament. In the normal cases the course of the reaction was very similar to the nickel

FIGURE XXI


$\Sigma\, d_1,\ d_2$ etc.
d_6
d_5
d_4
d_3
d_2
Time = SEC X 10^{-2}


$\ln(\theta_\infty - \theta_t)$
Time = SEC X 10^{-2}

catalysts but was slower so that the exchange of the final two hydrogens was not reached. Values of deuterium/hydrogen ratios agreed (within experimental error) with the final amounts of deuterium in the toluenes recorded in the mass spectrum. As no reaction went to completion the values of ϕ_∞ found on nickel films when using 10:1 mixture were adopted. Typical plots of log $(\phi_\infty - \phi)$ against t and % d_1, d_2 etc. against t are given in Figure XXI (Run 104). Energies of activation for side chain and ring exchange have been calculated to be 4 K.cal for side chain and 7 K.cal for ring exchange, but as mentioned earlier the accuracy of finding E is low. The number of moles of reactant exposed to the catalyst was, as before, 4.6×10^{-4} and 4.6×10^{-5} moles of deuterium and toluene respectively.

Infra-red spectra of the final products of each were recorded in CS_2 solution. Comparison of these with the summary in section 2,6 and with evaluated spectra of the products catalysed by nickel films revealed exchange to have occurred in the side chain and in the meta and para positions on the ring only.

Hydrogenation occurred to a small extent but total hydrogenated hydrocarbons never exceeded 0.5% of total hydrocarbons after 2 hours and was usually much less. The mass spectrum at 45 to 50 E.V. revealed the hydrogenated species and it was noted that the distribution of masses in the methyl cyclohexanes corresponded to the degree of exchange measured in the toluenes.

Results on poisoned films showed the course of the exchange in the side chain and gave values of N for this reaction. In Runs 89 and 104 the maxima in the methylcyclohexane mass spectra corresponded to an addition of 5.5D atoms to the toluene measured at the same time. (The deuterium was, by then, diluted with hydrogen from the exchange.). This results is held to indicate that no exchange occurred during the deuteration reaction.

TABLE VII

Summary of Platinum Films

Run	Weight	Temperature	Deuterium/toluene ratio
74 I	26 mgm	273	10.1
II	"	293 then 323	"
III	"	313	"
75 I	9.0 mgm	292	"
II	"	313	"
III	"	331	"
97	42 mgm	273	"
114	16 mgm	273	5.1

No rate constants were calculated, as accurate analysis was not possible.
(See page 88)

Section 3. 6

Results on Platinum films (with one negative result on copper)

These results are summarised in Table VII.

Platinum films were prepared with weights from 9.0 to 42 mgm. There was a considerable variation in reactivity amongst the films prepared but all which catalysed a reaction showed extensive deuteration and apparently slower exchange. The rate of hydrogenation made examination of the exchange difficult so that in Run 114 a mixture of 5 parts deuterium to 1 of toluene was used to slow down the relative reactions. Infra-red spectra of the products were taken particularly in Run 74 II when complete conversion appeared to have taken place, and the resulting strong peaks compared with those in the exchanged products on nickel so that peaks belonging to deuterated species could be differentiated from those belonging to exchanged species.

The mass spectra interfered with each other around m/e = 90 -92 when deuterium-containing cyclohexanes which have lost the methyl group interfere with spectra of toluenes which have exchanged one or two hydrogen atoms. Analysis by this means was therefore not possible.

In Run 74, I (273°K) deuteration was not expected and the slow rate of side chain exchange led to experiments at higher temperatures. In Run 74 II 293°K slow side chain exchange occurred with a gradual fall in total toluene present. The temperature was then raised to 323°K and left for two hours. After this period no toluene was found at 13 E.V. and scans at 45 E.V. and 16 E.V. established that complete deuteration had occurred. The distribution of peaks in the mass spectrum at 16 E.V. is quite regular around a maximum at mass 107 and extending from 102 to 112 and the series of peaks is repeated between masses 86 and 94 with the maximum at mass 89. Run 74 III was conducted at 313°K and scans were made at 16 E.V. to check the deuterated products as well as the exchanged products. Side chain

exchange was again found and a rate of ring exchange (presumably in the meta and para positions) equivalent to the apparent rate of deuteration. The relative proportions of the peaks at m/e = 93, 94 and 95 were not the same as those at m/e = 105, 106 and 107 there appeared to be more deuterium in the methylcyclohexanes, indicating exchange during or after the deuteration process.

Runs 73 I, II and III were similar to Run 74 III but reaction was very slow, probably because of the low film weight. Run 97 was very fast, again showing the characteristics of run 74 III. Run 114 showed side-chain exchange and slower deuteration which is reasonable in view of the reduced deuterium pressure. In this case the exchange rate was shown to be the side chain from the infra-red spectrum of the products.

A crude estimate of deuteration rate was possible in those experiments where complete conversion to methylcyclohexane had not occurred by measuring the final pressure of the hydrogens. This was found to be about 0.3%/min/10 mgm. Platinum at 293°K.

Copper film

An attempt to catalyse the reaction with a copper film of 30 mgm. (Run 93) resulted in no reaction at temperatures of 273, 293 and 313°K.

Section 3.7

The reproducibility and comparability of the results

The results on nickel and palladium films are numerous enough to estimate the reproducibility of the rates of the reactions studied in this system. On palladium at 275° rates vary from 0.66 to 1.6 x 10^{-2} atoms per 100 molecules per milligram per second. The higher value is associated with a higher value of M. The results on nickel are within a similar range. This range of values, roughly within a factor of three times the smallest result is the same as that obtained by Harper.[69] The work of Kemball and his co-workers should, therefore, be broadly comparable with the work reported here, but it should be borne in mind that the systems can not be completely comparable as Kemball used a reaction vessel of half the size of that used in our work and different initial partial pressures of reactants. Comment has already been made in Section 2,1 on the effect of pressure on the value of k_g deduced from the equations he uses. With these qualifications comparison of the data of this work with those of Kemball et al. is felt to be valid.

The incomplete reproducibility of the films may possibly be explained in the light of the work of Anderson,[70] who found that changes in the rate of metal deposition varied the activity of the films of nickel and tungsten. The films used for the experiments reported in this thesis were prepared by the standard methods outlined above but the degree of control of the deposition rate considered necessary by Anderson was not possible.

Indeed, films were used for the experimental work which had been produced from filaments which fractured during evaporation. The results on these films showed no large deviations from those where the filament did not fracture. However, a heavy local deposit was formed at the point where the break occurred and we have to conclude therefore that this lack of uniformity in thickness did not result in appreciable alteration of activity.

It would certainly have been helpful to have measurements of the film areas in order to try to relate them to the relative activities of films of the same metal, instead of relying on the surface area-weight relationships remaining constant in the range of film weights used. Such measurements (of area) would have been very difficult in the apparatus used because of the large dead spaces involved. The work of Porter and Tompkins [71] may be relevant to the difficulties experienced in attempting to make iron films. These workers found it necessary to reduce oxide layers on the wire with hydrogen and then removed occluded hydrogen by careful heating and cooling around 900°C, the α-γ phase-transition point. Retention of occluded gas can occur if this transition point is passed too quickly as the filament is freed from gas. The repeated recrystallisations which occur when Porter and Tompkins' method is used give rise to a fragile filament and they reported difficulty in avoiding breakages. Preparation of films by this procedure may give better results than those reported here but other workers, notably Kemball, appear to have obtained good results simply by evaporating the filament without previous reduction.

The rate of the deuteration reaction was estimated from the height of the peaks corresponding to methylcyclohexane observed at 45 electron volts. At this value it was considered that the relative sensitivity of the mass-spectrometer to toluene and to methylcyclohexane would be the same. (A.P.I. tables).[72] This rate could also be checked by a final measurement of total hydrogen and deuterium pressure. Except in the case of platinum the rates were too small to measure sufficiently accurately to yield accurate rate-constants but the relative deuteration and exchange rates could be estimated.

Section 4.1

General synopsis of data

The results of this work suggest that the reaction of toluene deuterium shows four distinguishable features:-

(i) exchange in the side-chain

(ii) exchange in the ring meta and para positions

(iii) exchange in the ring ortho positions

(iv) deuteration

The results obtained can be summarised as below:

(a) On Palladium

Side chain exchange rate> Ring - m.p. position exchange rate> deuteration rate.

Ortho exchange was not observed; and the methylcyclohexanes contained more deuterium than the simple addition of six deuterium atoms to the deutero toluenes observed at the same time. The ratio of the side chain exchange rate to the ring meta-para position exchange rate was about 100:1.

(b) On Nickel

Side chain exchange rate> Ring meta-para position exchange rate> ortho position exchange rate > deuteration rate

The ratio of the side-chain exchange rate to the ring meta-para position exchange rate was about 5:1 and the ratio of the ring meta-para exchange rate to the ortho position exchange rate was about 10:1.

(c) On Iron

Side chain exchange rate > Ring meta-para position exchange rate> deuteration rate

Very little ortho exchange was observed. Side chain exchange rates were about 100 times the ring meta-para position exchange rates. The methylcyclohexanes appeared to contain the amount of deuterium expected on the basis of addition of six deuterium atoms to the deutero-toluenes observed at the same time.

(d) On Platinum

It was possible to estimate relative rates by comparison of the mass-spectral data obtained on platinum films with those on other films. The estimated order would then be:-

Side chain exchange rate > Ring meta-para position exchange and the deuteration rate which were approximately equal.

The methylcyclohexanes contained more deuterium than the simple addition of six deuterium atoms to the deutero-toluenes observed at the same time.

The relative efficiency of the metals in exchange was

Nickel > Iron > Platinum > Palladium

and in deuteration was

Platinum> Nickel > Iron > Palladium

It should be noted that these are the same orders as Anderson and Kemball [26] for the benzene deuteration and exchange reactions.

Section 4.2

Discussion of Data

The synopsis given above contains various features which an acceptable mechanism must explain. These are:-

(a) Why side chain exchange always occurs before any of the other processes.

(b) The multiplicity of the side chain exchange.

(c) Why exchange of hydrogens ortho to the methyl group is difficult compared with those in meta and para positions.

(d) The variation in the relative ratios of side chain to ring exchange rates and deuteration rates to exchange rates from metal to metal.

(e) The effect of varying the initial ratios of deuterium to toluene on nickel films.

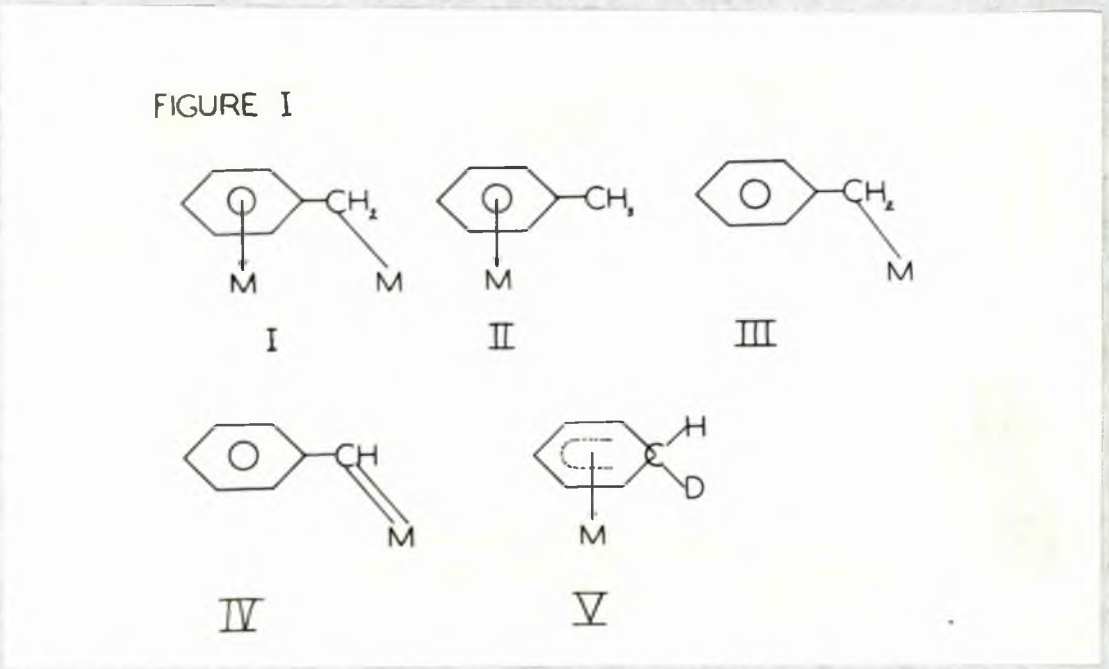
Further, any explanations will have to cope adequately with results already reported by Kemball and his co-workers on the reaction of deuterium with alkyl benzenes. Of this work the results of Crawford and Kemball on the effect of sintering on the rates of side-chain and ring exchange are of particular interest.

Section 4.3

The case of side chain exchange

The result common to all metals - the greater ease of side-chain exchange is the easiest for which to find an underlying cause.

FIGURE I



It is well known[1] that the bond dissociation energy $D(C_6H_5CH_2-H)$ = 84 kcal. mol^{-1} whereas the value for $D(CH_3C_6H_4-H)$ is probably about 103 kcal. $mole^{-1}$ from analogy with $D(C_6H_5-H)$. The precise way in which this greater ease of dissociation facilitates exchange depends on the mechanism one envisages for that reaction. If dissociation of a side-chain C-H bond and of D_2 are considered preliminaries to exchange i.e.

(a) $C_6H_5CH_3 + 2M \rightarrow C_6H_5CH_2-M + H-M$

(b) $D_2 + 2M \rightarrow 2D-M$

then it can be argued that (a) will be more readily achieved for a side-chain rather than a ring hydrogen.

This will not depend on any views as to whether the adsorption is purely single point as above i.e. when this side chain attachment is the only link (Figure 1, III) or whether the side-chain attachment is only one of the links (Figure 1, I) a particular molecule has to the surface. Thus ideas of multipoint adsorption or π-electron bonding could be associated with, for example, the difference in bond dissociation energies.

If the exchange is envisaged as a process where an adsorbed deuterium atom displaces a hydrogen atom in a side chain methyl group, (the molecule being held to the surface by methods other than attachment at the side-chain C atom), then this reaction would be easier for the CH_3 group than for the ring hydrogens.

This explanation of ease of side-chain exchange is the general view of Kemball[31,36] and his co-workers, of Garnett and Sollish[37] and of Hirota and Veda,[41] as summarised in the introduction for work on the exchange reactions of alkyl benzenes.

On this point the views of Crawford and Kimball[31] seem somewhat surprising in view of their data. They studied alkyl benzenes containing ethyl, isopropyl, and n-propyl substituents as well as methyl and obtained data for k_A (atoms per 100 molecules/per min/per 10 mgm. Nickel).

	Number of hydrogen atoms in groups			k_A	k_B	k_C	N
	A	B	C				
p-xylene	6	4	0	104	4	-	1.8
o-xylene	8	2	0	162	10	-	1.2
m-xylene	7	2	1	161	12	-	1.4
toluene (a)	6	2	0	67	5	-	1.4
ethylbenzene	5	2	3	92	3	0.9	1.0
ethylbenzene (b)	5	2	3	422	13	1.7	3.9
cumene (b)	4	2	6	90	11	4.0	1.7
n-propyl benzene (b)	5	2	5	137	7	2.0	1.6

(a) using twice the normal quantity of hydrocarbon

(b) at 0°C

The grouping of hydrogen atoms followed a consistent pattern.

Group A Hydrogen atoms on carbon atoms α to the benzene ring and atoms on the ring not ortho to a side group.

Group B Hydrogen atoms on the ring ortho to one but not two side groups.

Group C Hydrogen atoms on carbon atoms β and γ to the benzene ring.

They state (p.2463) that "there is relatively little variation in the reactivity of the hydrogen atoms on carbon atoms α to the ring." This is not substantiated by their data which we have quoted since the

k_A values at -10°C for o, m and p xylene and ethylbenzene range from 92 to 162. These figures also include some contribution from reaction of ring atoms in their definition of group A atoms.

Both associative and dissociative chemisorption can explain the side-chain exchange. Either (a) the side chain carbon-hydrogen bond is broken and the molecule becomes attached to the surface through the side chain i.e. classical dissociative adsorption (Figure 1,III) or (b) the molecule can be bound to the metal by the π electron system of the ring and the side chain attacked by a gas-phase deuterium molecule (Eley-Rideal mechanism) (Figure 1,II). Thirdly (c) they can be combined as Cranford and Kemball suggested (in Figure 1,I) the ring being bound to the metal by the π electron system and the dissociated side chain by a sigma bond. All these possibilities can explain multiple exchange. Although mechanism (a) has been discounted on palladium, it was found necessary by Harper and Kemball to explain the results on platinum and may make a small but significant contribution on palladium.

Kemball's views of the side-chain intermediates have changed with the increasing amount of data available, but the earlier and simpler suggestions of Cranford and Kemball are sufficient to explain the results obtained in this work.

The results obtained in Run 77 experiments I to IX showed a steady value of M of about 1.5 in reactions at 0°C and a decrease in the higher value of M (2.2 falling to 1.5) at 20°C as successive experiments were performed on the same film. This rise in the value of M with rising temperature had also been noted by Harper and Kemball. The multiple exchange process at higher temperatures is thus more easily poisoned and one explanation of this could be that the side chain exchange is a dual process involving the single exchange by dissociative chemisorption of the side chain on the one hand, and the multiple exchange in which the

ring is held by a π electron bond while the side chain is exchanged. Easier poisoning of π bonding sites is consistent with the views of Kemball that these are isolated sites of high activity.

Section 4. 4

The reactions of deuterium with the ring hydrogen atoms and the deuteration reaction.

The remaining features of the reactions studied are all concerned with the ring system. The results show there is a difference in the reactivity of the ortho positions compared with the meta and para positions which, in the case of the data on Palladium and Iron showed itself in the negligible rise of the d_7 and d_8 toluenes. The remaining feature of interest is the relationship of exchange rates in the side chain to that on the ring, and of ring exchange rates to deuteration rates. There again seems to be two possible mechanisms we can consider. The first is the simple dissociative process in which adsorption involves rupture of the ring carbon-hydrogen bonds and desorption occurs with formation of carbon-deuterium bonds. Studies on benzene showed values of N greater than one, so some two-point adsorption at least is necessary to explain multiple exchange. Anderson and Kemball[26] envisaged phenyl and phenylene intermediates.

These suggestions have the merit of simplicity, they do not require the destruction or use of the aromatic nuclei but they do not suggest any connection between the exchange and the deuteration reactions. The observed process with benzene appeared to show a gradual transformation from C_6H_6D to C_6D_6, and there did not appear to be any substantial formation of C_6D_6 initially or any connection of exchange and deuteration rates: Anderson and Kemball made specific mention of this point and also commented that the deuteration appeared to be direct addition of

six deuterium atoms to the deuterobenzenes observed at the same time. The catalytic metals which provided exchange and deuteration reactions at temperatures where the rates of both reactions could be measured were platinum and palladium. It must be said that the temperature range for these reactions with toluene and p-xylene on palladium and platinum is very similar but that both these molecules show evidence of exchange during deuteration. This indicates that exchange during deuteration may be a function of alkylbenzenes only.

Kemball revised his original mechanism of benzene exchange on the basis of the evidence of the greater effect on sintering on the ring exchange rates than on the side chain exchange rates on nickel. This he presumed indicated that there is a wide difference in the nature of the mechanism of the ring exchange and of the side-chain exchange - a pointer to the -bonded mechanisms found necessary to explain features of the exchange of cycloalkanes. It seems difficult to take evidence on one metal and apply it to results on others, especially as the results in this work have shown large differences between the behaviour of toluene reacting with deuterium on nickel and on palladium and platinum. Sintering is assumed by Kemball to have an effect on the number of sites responsible for bonding, but it could equally easily be contended that it altered the geometry of the film surface sufficiently to have excluded the possibility of formation of adsorbed phenylene biradicals, thus reducing the ring exchange rate by a considerable factor.

Although criticism can be levelled at their interpretation of the effect of sintering it remains a powerful piece of evidence for an associative interpretation.

The presence of strong deactivation of positions ortho to a side

group on the exchange reactions of alkyl benzenes is striking. The consensus of opinion seems to relate the effect to a steric or geometric factor. In considering the dissociative mechanism applied to toluene a study of models shows the effect of the side chain to be quite marked, both in preventing dissociative adsorption at the ortho position, and the "obstructive" effect of the side-chain on the local sites which could contribute adsorbed deuterium atoms to attack the ortho position. Simple blocking of the ortho position by the side-chain to an end-on attack by the deuterium atoms on the 2,3-di-adsorbed toluene molecule could also explain the relative reactivity of hydrogen atoms in this position. Garnett and Sollich's[37] work on the exchange of benzotrifluoride indicates that the effect is not due to electronic effects of substituents on the ring.

There is evidence for the presence of dissociated species on catalytic surfaces from the work of Suhrmann[29] and Gryaznov[30] who have reported the evolution of hydrogen when benzene is adsorbed on films of nickel, iron and platinum. This however is not evidence for the presence of such species as the reactive intermediates of the exchange reaction. Gryaznov [73] is on the point of publishing details of chemisorptive study of benzene on platinum and palladium films at room temperature. In this paper he suggests that methane can be produced on adsorbing benzene on a metal film inside a time of flight mass-spectrometer but the conditions are so different from those normally met with in an exchange process that it is questionable whether such evidence is relevant. It is not difficult to envisage a very short-lived weakly adsorbed surface species being the reactive intermediate in exchange reactions, but for which the only "evidence" is that it yields an easy explanation of the gas-phase products arising from the surface reaction with deuterium. Longer lived and

more strongly adsorbed species may give rise to direct evidence - as the production of hydrogen on benzene chemisorption indicates - but these may or may not be the reactive intermediates in exchange reactions.

The dissociative mechanism of exchange appears to be able to explain most of the data, with the merit of simplicity and without the necessity of the less well defined concept of π bonded intermediates. However, there is a steadily growing mass of indirect evidence making it necessary to consider such intermediates as possible additions or alternatives.

The Associative Mechanism

The second mechanism of deuterium exchange is the reaction of a species associatively adsorbed on the surface by interaction of the π electrons of the ring with d-orbitals of the metal atom or with the degenerate d-electron bonds of the metallic crystal. Reaction can then occur by the Langmuir or Eley-Rideal mechanisms. In the Langmuir mechanism a chemisorbed deuterium reacts with the chemisorbed toluene, presumably expelling the hydrogen atom from the toluene and replacing it with the adsorbed deuterium atom. In an Eley-Rideal mechanism reaction between a gas-phase deuterium molecule and an adsorbed toluene molecule forms the exchanged species.

The utility of such species in explaining some aspects of exchange of alkyl benzenes has been mentioned above. A direct analogy with organo metallic compounds is possible since the range of stability of bisbenzene compounds decreases towards the end of the transition - metal series, suggesting that the π bonded intermediates would be suitably short-lived on the surface.

On the other hand Völter[74] has shown a relationship between the energies of activation for the hydrogenation of benzenes and alkyl

FIGURE II

FIGURE II

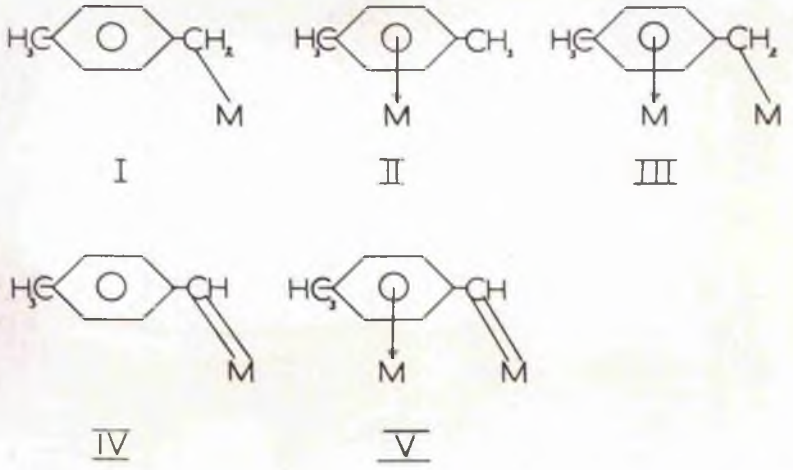
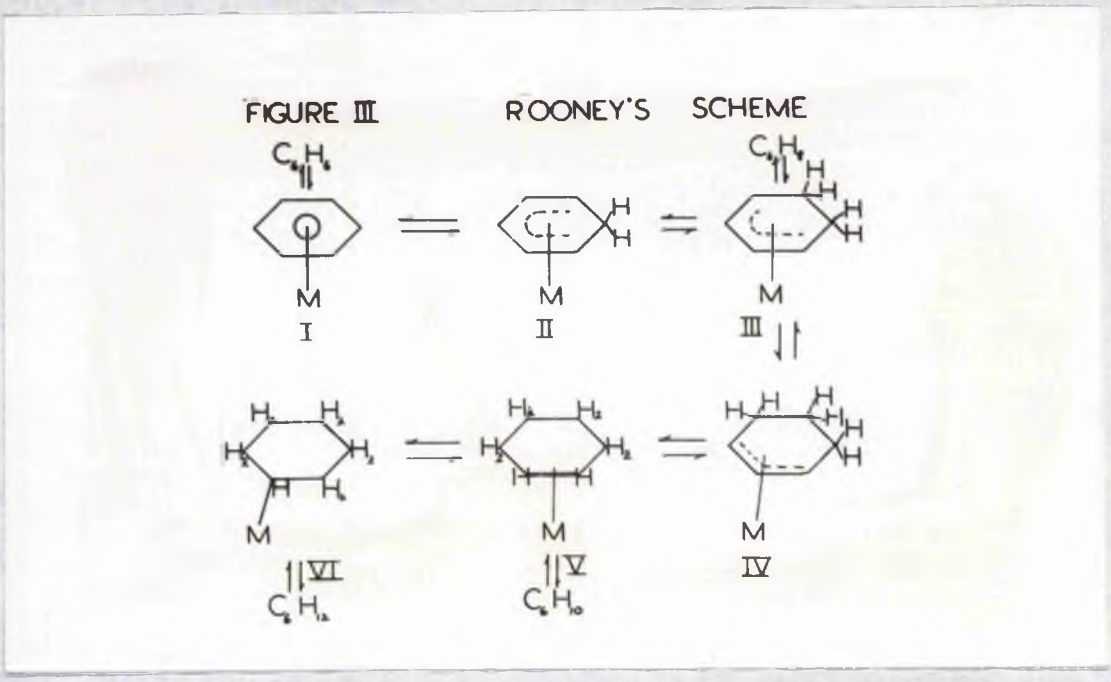


FIGURE III



benzenes and the greater stability of the corresponding bisbenzene organometallic compounds. He considers stronger adsorption to be necessary to facilitate hydrogenation. Kemball[76] has resuscitated the old idea that reactive sites are single atoms raised above the surface plane, attached to only a few near-neighbours. Under these conditions the d orbitals may still have some of the geometric shape attributable to the single atom. The work of Kemball and Crawford on sintering is then seen as a removal of such sites into a metallic crystal structure. This sintering evidence has been extended by Phillips, Crawford and Kemball[77] who examined the effect of carbon monoxide gas as ligands on the sites giving the greatest heat of adsorption. The reduction of rate of side-chain exchange in p-xylene by a factor of three was matched by a fall in rate of ring exchange by a factor of 100 on carbon monoxide treated catalysts. The authors infer a removal of the special "metastable atom" sites and view such sites as able to form bonded intermediates.

Harper and Kemball's[36] evidence for exchange during deuteration of p-xylene particularly on palladium films suggested the mechanism put forward by them and outlined above in Section 1. It is extremely complex, involving both Langmuir and Eley-Rideal mechanisms but these are, apparently, considered necessary to explain the mass of conflicting evidence on benzene and alkyl benzene exchange. These ideas can be applied to the reaction of toluene with deuterium. For simplicity the side-chain will be excluded.

1) Exchange is explained by formation of the intermediate suggested by Hartog et al.[32] and further intermediates suggested by Rooney[24] which are shown in Figure I, V and Figure III.

2) Stepwise interconversion of these species may occur by a deuteration (or reverse) reaction involving addition or removal of

hydrogen from the surface side of the plane of the ring. This involves a chemisorbed hydrogen in a Langmuir mechanism, and conversion of an Sp^2 hybridised carbon atom to Sp^3 and vice-versa, alternatively the intermediate could react by the Eley-Rideal mechanism but since they revert to the Sp^2 hybridised state the "extra" deuterium atom is lost and the product contains only one deuterium atom.

3) Additionally, intermediates I to V in Rooney's scheme (Figure III) may undergo exchange by the Eley-Rideal process involving the hydrogen atoms on the opposite side of the plane of the ring to the metal surface.

Exchange reactions can only occur by a reverse of the other process, diagrammatically

$$\underset{M}{D} + [\underset{M}{C_6H_5H}] \rightleftharpoons [\underset{M}{C_6H_5\overset{H}{D}}] \longrightarrow [\underset{M}{C_6H_5D}]$$

Langmuir

$$D_2 + [\underset{M}{C_6H_5H}] \rightleftharpoons [\underset{M}{C_6H_5\overset{D}{H}}] \longrightarrow [\underset{M}{C_6H_5D}]$$

Eley-Rideal

The Sp^3 hybridised atom may return to the Sp^2 state by either mechanism, and where this follows the other process exchange occurs. Deuteration can only occur by a Langmuir process and multiple exchange by a series of conversions between the Sp^2 and Sp^3 hybridised states before desorption.

Deuteration

Formation of intermediates of types III, V, and VI (Figure III) could give rise to deuterated hydrocarbons in the gas-phase containing two, one or no double bonds. In these cases the Sp^3 hybridised carbon atoms remain in this state and the extent of the Eley-Rideal exchange during the deuteration process will be apparent from the deuterium content of the gas-phase material.

π bonded mechanism

The extent of such exchange during deuteration on palladium led Kemball and Harper to suggest this mechanism; they found the initial mean deuterium content of the 1,4-dimethylcyclohexanes to be 13.19 (total "hydrogen" atoms = 16) with a maximum in the initial distribution around the d_{13} d_{14} and d_{15} 1.4 dimethylcyclohexanes.

This reaction was carried out at 70° at which temperature, however, as Table I shows, extensive multiple exchange of methylcyclohexanes is known to occur. Consequently the complexities of his explanation may seem unnecessary. The simple dissociative mechanism would explain these processes in terms of the usual α-β process for ring exchange with replacement or addition of hydrogen atoms as alternative and possibly competing processes. The 1,4-dimethylcyclohexane or intermediate olefins formed could then undergo multiple exchange by an α - β process. The alternative associative mechanism explains some features of the alkylcyclohexane exchange in a more satisfactory way [22,23] so that this cumbersome mechanism of Harper and Kemball must be considered as an alternative but more evidence is clearly necessary before the mechanism is established unequivocally.

The application of this associative mechanism to the results obtained (in this work) is relatively simple. It appears that the formation of the intermediate suggested by Hartog et al will explain the ring exchange process, it being reconverted to deutero-toluene

after exchange. The relative possibility of forming further intermediates differs from metal to metal. Thus on nickel exchange can be said to occur throughout the molecule before deuteration sets in if the step of forming intermediates III, IV etc. in Rooney's scheme is very difficult compared with the ease of return to aromatic hydrocarbon. On palladium and iron the formation of II and IV has to be postulated as being easier than the formation of the ortho-exchanged intermediate. On platinum addition of deuterium occurs at the same rate as exchange in the meta and para positions indicating greater ease of formation of intermediates III, IV, V and finally VI on this metal. It can be assumed that with the large excess of deuterium deuteration will be a preferred process once the electron system contains fewer than 4 electrons.[66]

One can speculate on reasons for the variation of the relative ratios of rate constants for side chain and ring exchange. On nickel the side-chain exchange rate constant is only twice that of ring meta and para positions, while on palladium and iron the ratio is 100:1.

If the difference in rates was purely due to the difference in C-H bond energies in the side-chain and ring positions the relative rates should be similar on all metals. Since this is not what has been observed it is necessary to seek differences between the metals which will aid an explanation. The correlation of metal proper with catalytic activity have been attempted widely in the past and a recent survey is available[11], admittedly largely concerned with the hydrogenation of ethylene. However, the criteria surveyed such as atomic radius, percent d character etc. do not enable palladium and iron to be paired, as required for our reaction, and to be marked off from nickel.

It is possible, however, that a search for a correlation between metal properties and their activities as catalysts is taking too simple a view. If a nickel film is sintered the ratio of side-chain to ring

activity is altered until it is similar to the values for fresh films of iron and palladium. It is possible that the latter already have physical structures which do not favour ring exchange. From this viewpoint the most one can postulate is that the processes of side-chain and ring exchange probably involve different mechanisms.

It is argued by Kemball, and collaborators, that the π bonding concept together with the 6 stages of intermediate formation in Figure III can explain the observed phenomenon readily. This is evidently the case, since there are many adjustable parameters, but until it is possible to specify the reasons for the differences in metal behaviour more accurately the picture presented can be said to rest on little more than reasonable conjecture. To illustrate the flexibilities of their picture we can translate our findings into their terms. On nickel, using the associative adsorption picture, toluene is easily adsorbed by binding the π -electron system to the metal, but only the intermediate containing one Sp^3 hybridised atom is easily formed, and this process is only slightly more difficult than exchange of a side-chain deuterium atom. On palladium simple side-chain dissociation occurs more easily than the formation of the species causing ring exchange, but when these are formed movement through the range of species to the deuterated product is easier than on nickel. On platinum movement through this range is much easier giving rise to earlier deuteration.

It is then a question of the ease of transformation of species II of Rooney's scheme to species III and further species, or reversion to species I. On nickel species III is difficult to obtain compared with the reversal to species I while on palladium III is slightly more easily obtained and on platinum much more easily obtained. This may be a valuable picture but it is not possible to calculate these relative reactivities from information independently obtained, and so the picture is conjectural only.

The Combination of Associative and Dissociative Mechanisms

Garnett and Sollish [37] have combined the associative and dissociative mechanisms in order to explain the exchange by a dissociative mechanism and deuteration by an associative mechanism. It will explain Garnett's evidence completely, particularly with regard to the difficulty of exchange in the ortho positions and in many ways is a useful compromise.

Summary on Ring Exchange

Clearly both associative and dissociative mechanisms can explain the exchange reactions of toluene with deuterium. There appears to be no reason for excluding one in favour of the other, so that both may be operative at any time. Evidence can be advanced for the presence of either species and insufficient data are available for one to be completely certain of the mechanism of these processes.

Section 4.5

The effect of varying the pressures of the reactants on the reaction-rate on nickel films

The results show that in the range of pressures chosen the effect of increasing deuterium pressure on the reaction rate is small, but that it does not increase the rate. It would therefore appear that the metal film surface is nearly covered with chemisorbed deuterium at the original pressure and would not affect the surface concentration of adsorbed deuterium atoms.

When the toluene pressure is increased the rate is reduced, even when allowance is made for the fact that the reaction is followed by the change in the deuterium content of the toluene. This is not the same effect as that found by Anderson and Kemball [26] for the effect of varying pressures on the rate of the exchange reaction of benzene on platinum and palladium ($R_B \propto P_{Bz}^{0.1} P_{D_2}^{-0.5}$). It is assumed that this effect is due to the formation of a strongly adsorbed toluene species which successfully

competes with deuterium for the available sites on the catalyst surface. Anderson [66] has investigated the hydrogenation reaction on nickel films at 45°C and commented on the poisoning effect of methyl cyclohexane residues on the surface. In this work extensive hydrogenation was not found but alkanes could have been present on the surface in sufficient quantity to partially poison the reaction without being detectable in the gas phase, but this possibility seems very slight.

If this interpretation is acceptable, i.e. that toluene is preferentially adsorbed and displaces reactive chemisorbed deuterium, it can easily be envisaged as a flat adsorption of toluene removing a large number of sites available to the deuterium per molecule of toluene adsorbed.

Useful information could be gained from a further comparative study of the effect of pressure changes of this kind and the precise effect on other metals could be compared. This could throw light on the relative properties of adsorbed species on the surface and the way this changes from metal to metal.

Section 4.6

The infra-red spectra of adsorbed species

Eischens [78] and his co-workers have established methods of determining some aspects of the intermediates formed in catalytic reactions, by direct examination of the species in infra-red spectrometers. The sample of catalyst, usually metal supported on silica is prepared in a vacuum-tight apparatus and the progress of some reactions can be followed using this technique. It was hoped that results might be obtained when benzene or toluene were exposed to suitably prepared palladium or nickel catalysts mounted in the beam of the spectrometer. Two supports were used, a high area silica powder compressed into a disc, and vycor porous glass. The latter material was suggested by the work of Sheppard.[79] This technique exposes the region of carbon-hydrogen stretching absorption around 3μ.

Repeated experiments showed the presence of the strong physical adsorption of toluene on silica already known to occur.[80] Heating and pumping the material removed all traces of hydrocarbon without any bands equivalent to chemisorbed materials becoming visible. Eischens[81] and Blyholder[82] have also experienced these difficulties and obtained similar, negative results. The method has large experimental difficulties and it may be that some new technique may make such spectra available. Even so, they may only confirm the long-lived species which may not be those responsible for the reaction steps outlined above.

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